

CHEMICAL ABSTRACTS

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1—APPARATUS

C. G. DERICK

New aids for Röntgen-spectroscopy. (I), (II). A mercury-vapor jet-pump of steel. (III) Vacuum spectrograph for the region of the ultra-violet and Röntgen rays. (IV) Space-lattice models with separable parts. HUGO STUNTZING. *Physik. Z.* 23, 463-74(1922).—These aids are intended to simplify the use of X-ray methods in scientific institutions and in factories. The high-speed Hg-vapor pump is made of steel and has provisions for regulating the heat supply, for purifying the Hg when necessary, and for easy cleaning and reassembling. The high-vacuum spectrograph is designed for use in all of the various methods of spectroscopy with visible, ultra-violet, and X-ray radiation. The spectrograph chamber is entirely surrounded by an oil-bath which renders all joints vacuum tight and provides for temp. control. The original paper should be consulted for the structural details which include provisions (a) for easily renewing the filament of the attached X-ray tube, (b) for allowing the current to pass only at intervals corresponding to definite positions of the crystal table, and a new method of adjusting the crystal. Space-lattice models of calcite and of S's arrangement of the periodic system (cf. *C. A.* 11, 552) are illustrated. These models were constructed of parts designed for the building-up of any desired space-lattice structure.

C. C. VAN VOORHIS

The light valve. F. E. LAMPLUGH. *Illum. Eng.* (London) 15, 63-4(1922).—In the light valve volatile liquid and vapor of the liquid are contained in 2 connected glass bulbs which are supported on a frame. This is free to rock on pivots and is connected by levers to the valve itself. One of the bulbs is blackened and the other is left transparent. The blackened bulb, even in comparatively weak daylight, reaches a temp. sufficiently in excess of that of the other bulb (0.1-0.2°) to cause appreciable relative increase in the vapor pressure of the liquid. A head of liquid therefore develops in the transparent bulb by distn. of liquid from the blackened bulb, and the frame is caused to rock over and close the valve.

C. G. F.

Apparatus for photomicrography. G. DURANTE. *Compt. rend.* 175, 1201-3 (1922).—The app. described differs from the customary app. in that the source and microscope are hermetically sealed so that light cannot pass except through the ocular. A lamp with V-shaped filament gives a point source, all posterior rays being reflected by means of a spherical mirror. A rheostat affords adjustment for 8 different light intensities. Mirror, lamp, and condenser are enclosed in a jointed tube. The camera has the form and dimensions of a microscope case, through the top of which passes the ocular tube. The plate holder can be moved up or down on a rigid tube which is screwed on to the case but is demountable. The app. is readily portable, simple in operation, reasonable in cost, and has no bellows to limit size of exposure; by simple alignment of the plate, a strong magnification with feeble objectives is possible. With but small magnification, an image can be obtained at a distance of 2 m., which is bright enough to be seen readily by a limited audience.

T. F. BUEHRER

Melting-point tubes as reaction vessels. AUGUST FUCHS. *Monatsh.* 43, 129-37 (1922).—Details are given for the common lab. manipulation, using 2-5 mg. of material,

including crystn., washing and drying, sublimation, etc. That satisfactory preps. and purifications can be carried out in m.-p. tubes is shown by the examples actually worked out.

C. J. WEST

A new adjustable thermostat for all temperatures between 0° and 100°. S. J. LEWIS AND FLORENCE M. WOOD. *Trans. Faraday Soc.* 17, 696-702(1922).—A detailed description of a 20-gal. thermostat which maintained a temp. const. to 0.01°. The water was covered with a layer of heavy paraffin to prevent evapn. and to act as an insulating medium. The thermoregulator is readily adjustable by steps of 1°, ranging up to 100°.

DWIGHT T. EWING

Demonstration of a new Gaede diffusion-pump. ALFRED SCHMIOT. *Physik. Z.* 23, 462-3(1922).—The construction of this high-speed steel pump is to be described later.

C. C. VAN VOORHIS

Generator for producing acetylene under pressure for the chemical industry. ANON. *Z. angew. Chem.* 36, 56(1923).—A description, with 2 cuts, of the "Weko" app. for producing C_2H_2 under pressures up to 1 m. H_2O .

J. H. MOORE

A new form of ozonizer. II. NĚMEČEK. *Chem. Listy* 16, 276(1922).—Two stout copper wires serve as electrodes in a horizontal glass cylinder, the arrangement being such that the distance between the electrodes can be varied. The energy can be obtained by means of a Ruhmkorff's coil or an elec. machine.

J. C. S.

An efficient reflux air condenser. G. T. DOUGHERTY. *Ind. Eng. Chem.* 15, 338(1922).

E. J. C.

A laboratory fractionating column. H. T. CLARKE and E. J. RAHRS. *Ind. Eng. Chem.* 15, 349(1923).

E. J. C.

A new apparatus for washing gases. A. ERNST. *Chem. Listy* 16, 274-6(1922).—The tube leading the gas to be purified into the washing bottle is surrounded by a long spiral, along which the gas has to make its way and is thus well washed. The tube leading in the gas and the spiral are easily removed from the vessel.

J. C. S.

A simple apparatus for the determination of benzene in gases by means of active carbon. TH. HABER. *Chem.-Ztg.* 47, 62(1923).—A description of Bunge's app., which consists of a Cu cylinder contg. 100 g. C capable of adsorbing 20 g. C_6H_6 . The gas, freed from dust and S , passes in at the top and out at the bottom through a tube wound S or 10 times around the cylinder, thence to the meter. The C_6H_6 is removed from the C by heating the app. to 170° in an oil bath and passing steam through in the reverse direction. The steam and C_6H_6 may be condensed and the vol. of the C_6H_6 measured. Cf. C. A. 16, 450, 2374, 4050.

J. H. MOORE

A simple apparatus for determining carbon in iron, steel, etc. G. LĚGALL, DU TERTRE. *Technique moderne* 15, 86(1923).—A simple app. is described in which the CO_2 obtained from a sample of iron or steel by oxidation in the wet way is absorbed in NaOH soln. and the CO_2 detd. by the loss in vol. It consists of a 300-cc. tube, graduated in 0.5 cc., sepd. by an ebonite cock from a reservoir of about 75 cc. capacity for the excess NaOH soln. The graduated tube is filled with water and the CO_2 is bubbled into it. After the vol. of gas is read with the usual precautions, the CO_2 is absorbed in NaOH and the vol. of residual gas detd.

W. T. H.

Apparatus for the recovery of bromine from sodium hypobromite. C. H. COLLINGS. *Chem. News* 126, 55-8, 95(1923).—From waste NaOBr solns. used in urea detns. Br is recovered by acidifying and passing a stream of air through the soln. and then into NaOH in which the Br is absorbed, regenerating NaOBr. Because less heat is evolved than in the usual method whereby liquid Br is added to NaOH soln., there is less $NaBrO_3$ produced and the NaOBr soln. is more effective. The O in the stream of air used may cause the reaction: $2Br_2 + O_2 + 4NaOH = NaBr + 2NaOBr + NaBrO_2 + 2H_2O$. The app. is described.

M. O. LAMAR

A new absorption bottle for carbon dioxide and moisture. WM. E. MORGAN. *Ind. Eng. Chem.* 15, 266(1923). Correction. *Ibid.* 429. E. J. C.

Volt-ampere meters (FRYER) 4.

Filter. M. KESSLER. U. S. 1,446,187, Feb. 20. The filter is made up of filtering layers alternating with inlet distributing plates having air discharge channels.

Scleroscope. T. A. HALL. U. S. 1,446,620, Feb. 27. A portable scleroscope, provided with a rebounding hammer within a tubular casing, is constructed so as to be invertible.

Sublimation apparatus. L. L. JACKSON. U. S. 1,446,564, Feb. 27. An app. adapted for the sublimation of *resorcinol* is formed with a vaporization chamber connected to a condensing chamber and with a return conduit from the condensing chamber back to the heated vaporizing chamber so that uncondensed gas may be continuously circulated between the vaporizing and condensing chambers.

2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

Recent advances in science. Physical chemistry. W. E. GARNER. *Science Progress* 17, 195-9(1922).—Review of recent work on the ionization theory of Ghosh and on the constitution of metallic substances. *Ibid.* 357-61(1923).—Review of recent work on chem. reactivity and on liquid-crystal formation and chem. constitution.

JOSEPH S. HEPBURN

Recent advances in science—Physics. J. RICE. *Science Progress* 17, 190-5 (1922).—Discussion of a quantum mechanism in the atom. JOSEPH S. HEPBURN

Arabic chemistry. E. J. HOLMYARD. *Science Progress* 17, 252-61(1922).—A study of the Arabian chemists, their texts, theories, app., and work. The Greek influence was marked in the early days, at least, of Arabian alchemy. The fundamental conception was the unity of matter, hence the transmutation of the metals was considered possible; two elixirs were recognized, the red elixir to convert Ag into Au and the white elixir to convert the other metals into Ag. The importance of accurate weighing was stressed; yet change of wt. during a chem. reaction either was not observed or was not considered of much importance.

JOSEPH S. HEPBURN

Scientific pictures of Joseph Wright. P. W. SHURLOCK. *Science Progress* 17, 432-8(1923).—Contains a reproduction and full description of Wright's painting of The Alchymist and the discovery of P.

JOSEPH S. HEPBURN

Franklin Bache, Chemist. EDGAR F. SMITH. *Brochure*, 15 pp., Philadelphia, 1922.—A sketch with portrait of the life of Bache (1792-1864) and of his contributions to chemistry.

JOSEPH S. HEPBURN

James Curtis Booth, Chemist. EDGAR F. SMITH. *Brochure*, 17 pp., 1922.—A sketch, with portrait, of the life of Booth (1810-1888) and of his contributions to chemistry and geology, including the foundation of a lab. of practical chemistry, work as melter and refiner of the Philadelphia Mint, and service as president of the American Chemical Society 1883-1884.

JOSEPH S. HEPBURN

Determination of the atomic weight of boron (preliminary communication). ALFRED STOCK AND ERNST KUSS. *Ber.* 56B, 314-6(1923).—The at. wt. of B was detd. by measuring the vol. of H_2 evolved when the gas *disboran*, B_2H_4 , is decomposed quant. by H_2O : $B_2H_4 + 6H_2O \approx 2H_3BO_3 + 6H_2$. Independently detd. values of the at. wt. are: 10.810, 10.804, 10.803, 10.802, 10.810, 10.804; mean, 10.8055 ± 0.0015 . This is lower than recent values based on the analysis of BCl_3 , 10.82-10.84. A very

preliminary detn. of the at. wt. of Si, made by measuring the vol. of H_2 evolved in the reaction, $SiH_4 + 2NaOH + H_2O = Na_2SiO_3 + 4H_2$, gave a value of about 28.15, and indicates that the accepted value, 28.3, is too high. Details of the work on B will be published in the *Z. anorg. allgem. Chem.*

R. H. LOMBARD

Compressibility, internal pressure and atomic magnitudes. T. W. RICHARDS. *J. Am. Chem. Soc.* 45, 422-37(1923).—With the help of results already obtained on the compressibilities of Cl and Br and Bridgman's pressure-vol. curves for Na and K, values for the av. internal pressures existing in the salts of these elements, and the relative vols. and the at. diams. of the components have been calcd. and many conclusions drawn from the results. The av. internal pressures in KCl, KBr, NaCl and NaBr are 65000, 54000, 100000, and 85000 kg./cm.², resp. The values for the at. diams. differ but slightly from those previously found. (*C. A.* 16, 180.) The coincidence from 2 entirely different exptl. methods of evaluation gives the greatest possible weight to these dimensions.

H. JERMAIN CREIGHTON

The new element hafnium. D. COSTER AND G. HEVESY. *Nature* 111, 182(1923); cf. *C. A.* 17, 923.—By the addn. of a known quantity of Ta to the samples and comparing intensities of the Ta and Hf lines, it is found that all Zr minerals investigated, from whatever source, contained 5-10% Hf. [Surprising in view of the negative spectroscopic and chem. results of Hauscr and Wirtb, *C. A.* 4, 872, 2421, and 3056.—ABSTR.] One sample of conu. ZrO_2 showed 5% of Hf. From this were prepd. several g. of material showing 50% Hf. Conversely Zr has been prepd. which shows no Hf lines.

NORRIS F. HALL

The crystal structure of beryllium and beryllium oxide. L. W. MCKEEHAN. *Proc. Nat. Acad. Sci.* 8, 270-4(1922).—The Be was obtained by electrolysis of sodium beryllium fluoride, $2BeF.Na_2F$, and contained a few % of BeO. The diffracting centers in the metal and its oxide lie at the points of two symmetrically interpenetrating hexagonal space lattices. For BeO, the axial ratio, $c/a = 1.63$, and $a = 2.696 \times 10^{-8}$ cm.; for Be, $c/a = 1.58$ and $a = 2.283 \times 10^{-8}$ cm. These values give computed ds. within 1% of the best previous values. Be more closely resembles Mg, Zn and Cd, than Ca, Sr, and Ba; the oxide is an analog of ZnO, and the structure suggested by W. L. Bragg (*C. A.* 14, 3585) for the latter substance is also possible for BeO. J. C. S.

The atomic arrangement in the optically active crystals, sodium bromate and sodium chlorate. L. VEGARD. *Z. Physik* 12, 289-303(1922).—The difference in structure between $NaClO_3$ and $NaBrO_3$, which are optically active, and the nitrates of Pb and the alk. earths when anhydrous, which are optically inactive but which crystallize in the same class as the first 2 salts, lies in the position of the O atoms, as shown by spectrographs. In the nitrates the 3 atoms of O form a triangle in a plane normal to the line joining the at. centers of the metal and the N but placed between these two centers. In the halogen salts considered the halogen atom lies between the metal and a plane similar to that in the nitrates contg. the O atoms. A. E. STEARN

Further growth of metal crystals by separation from the gaseous phase. F. KOREF. *Z. Elektrochem.* 28, 511-7(1922).—The further growth of metal crystals can be carried out in other ways than by the decompn. of volatile compds. of metals. Under suitable conditions the metal vapor can be pptd. as crystals. The paper contains a no. of excellent photomicrographs showing the progress of the growth of crystals pptd. from metal vapor.

H. JERMAIN CREIGHTON

Unusual crystals. G. H. MARTYN. *Nature* 111, 186(1923).—Description of thin-walled tubular crystals of phenol spontaneously formed from supersatd. vapor on outside only.

G. I. CLARK

The occlusion of hydrogen in palladium. MIYUO YAMADA. *Phil. Mag.* 45, 241-3(1923).—X-ray spectrograms were made of a Pd wire 0.5 mm. in diam., (1) in

its original condition, (2) after it had electrolytically occluded 660 times its own vol. of H_2 , which corresponds to a 29% mol. mixt., resulting in an expansion of 2.9% by direct measurement of its diam., or 2.8% as calcd. from the spectrogram. The only difference to be noted in the two spectrograms is a slight contraction of the intervals after the occlusion of H_2 , due to the uniform expansion of the space lattice. It is concluded that compd. formation is not indicated and that H is absorbed in solid soln.

S. C. LIND

The chemical constants of the halogens in the monatomic and the molecular states. F. A. HENGLEIN. *Z. Physik* 12, 245-52(1922).—The Stern-Tetrode equation for the chem. const. of a monatomic gas, $C = -1.60 + 1.5 \log M$, where M is the mol. wt., was found to hold for the monatomic halogens except I, for which it gave a value 20% too high. This was thought to be due to inaccuracy in v. p. data for I from which C was obtained, rather than from the fact that the above equation is not adequate. The values of C calcd. from dissociation equil. and v. p. curves, are as follows: I_2 , 2.55; Br_2 , 1.50; NO , 0.92; O_2 , 0.80; Cl_2 , 0.02; N_2 , -0.05; CO_2 , -0.41; NH_3 , -2.45; H_2 , -3.77.

A. E. STEARN

Pressure of saturated carbonyl chloride vapor. N. I. NIKITIN. *J. Russ. Phys. Chem. Soc.* 52, 235-49(1920).—The vapor pressure of carefully purified $COCl_2$ has been measured at a no. of temps. ranging from 12.6° to -99° . The pressure has the value 889.2 mm. at 12.6° , and diminishes rapidly with fall of temp. to 540.4 mm. at -0.41° , and then continually more slowly; at -19.43° the value is 232.2 mm. and at -94.2° a few tenths of a mm.

J. C. S.

Velocity of vaporization regularities. W. HERZ. *Z. Elektrochem.* 28, 526-7(1922).—Since the velocity of vaporization, $G = (1/\sqrt{2\pi R})p\sqrt{M/T}$, it follows that G varies directly as $\sqrt{M/T}$ at the b. p. (T). Values for $\sqrt{M/T}$ show that in homologous series of org. compds. G increases with the mol. wt. The substitution of OH for H in aliphatic hydrocarbons decreases the value of G , while substitution of halogens in hydrocarbons and acids brings about an increase. The introduction of double and triple bonds decreases G , thus $G_{\text{propane}} > G_{\text{propene}} > G_{\text{propyne}}$.

H. JERMAIN CREIGHTON

Viscosity. W. H. HERSCHEL, et al. *Proc. Am. Soc. Testing Materials* 22, Pt. I, 423-4(1922).—Report of sub-committee. A table of approx. relations between Saybolt Universal times and Saybolt Furol times is given. Above 200 seconds Furol, the ratio Saybolt Universal/Furol is 10:1.

W. F. FARAGHER

Refractive indices and their temperature coefficients. GARTHA THOMPSON. *Pharm. J.* 110, 26-7(1923).—The Brit. Pharm. 1914 gives a uniform temp. coeff. of ± 0.00038 for all substances for temps. below or above 15.5° . This no. is quite true for fixed oils, but not even approx. true for many other classes and substances. For essential oils it is about 0.00045; for benzene 0.00062 (20°), 0.00067 (70°) (cf. *C. A.* 16, 2131). Many more examples are given to show that the value of the temp. coeff. depends on the nature of the substance.

S. WALDBOTT

Theory of absorption processes. A. EUCKEN. *Z. Elektrochem.* 28, 257-8(1922).—Polematical against Polanyi (*C. A.* 16, 3874).

H. JERMAIN CREIGHTON

Adsorption at liquid-vapor and liquid-liquid interfaces and some related phenomena. H. H. KING. *Kansas Agr. Expt. Sta., Tech. Bull.* 9, 39 pp.(1922); cf. *C. A.* 16, 3783.—The adsorption was calcd. by plotting surface tensions at varying concns. against the log of the concn. and applying the Gibbs equation. In detg. surface tension by the drop-wt. method the wt. of a hanging drop was found to depend upon its time of formation, explanation being found in the application of Pick's law. The adsorptions in the liquid-vapor interface in moles per sq. cm. and likewise the no. of mols. area occupied by each and their daims. are given for the 1st 10 acids of the aliphatic series, and several

alcs., amines and esters. Comparison of the log curves of the acids and alcs. shows that the latter exhibit a greater adsorption than the former and also possess a const. degree of adsorption through a greater range of concn. change. Explanation may be found in the different electrolytic characters of the acids as compared with the alcs. Alcs. of 4 and 5 C atoms reach zero adsorption at the same concn. as do acids of the same no. of C atoms; alcs. of 1, 2 and 3 C atoms show adsorption at lower concns. than do the corresponding acids. The curves for the esters lie very nearly in the same position as those of the alcs. of the same no. of C atoms; and taken as a whole they correspond closely to those of the acids. Et propionate and Pr acetate show an interesting relation in that the former requires a higher concn. to produce the same adsorption. The more sym. the ester the smaller the adsorption after it has once become const. Expts. with butyric acid solns. showed that the fugacity of the mols. in the interface $H_2O-C_6H_6$ is 3 times as high as on the surface of H_2O , when both films have the same concn. of about 10^{14} mols. per sq. cm. The adsorption of substances of the type of org. acids, alcs. and esters is always greater at the surface of H_2O than at the interface between H_2O and an org. solvent of the type of C_6H_6 or a paraffin. Evidence is given to show that single mols. of butyric acid are more sol. in H_2O than in C_6H_6 , but that the double mols. are more sol. in C_6H_6 . The presence of C_6H_6 as an upper layer does not change the no. of butyric acid mols. in this monomol. layer. P. R. DAWSON

Solutions, suspensions, colloids. N. P. PESKOV. *Bull. Inst. Polyt. Ivanovo-Voznesensk* 6, 73-99(1922).—The theoretical considerations developed by P. lead to the following conclusions. The modern doctrine of colloids deals with a conception of heterogeneity which is totally different from that assumed by the doctrine of phases, but is identical with the mol.-kinetic view of the universe; the latter is termed the generalized conception of heterogeneity. The notion of dispersion current in the chemistry of colloids must be regarded as composed of two different conceptions, distinguished as qual. and quant. dispersion. The former of these is synonymous with the generalized conception of heterogeneity referred to above, and has no special bearing on systems represented by suspensions, colloids, and solns. The latter, possessing a dimensional character, differs from the idea of a phase only in that the latter is characterized by the spacial magnitudes of its sep. elements. Thus all systems to which the term quant. is applied must be considered to be polyphasic. Phys. theories of colloids in general postulate that: (1) suspensions, colloids, and true solns. are systems, the qual. differences between which may be regarded as functions of their degrees of dispersion; (2) colloids represent typical polyphase systems; and (3) all the characteristic properties of colloids are merely the results of the magnitudes of the mols. The logical objection to such theories is that they accept as results of the doctrine of dispersion the hypothetical assumptions on which this doctrine is based. Only careful investigation, from all points of view, of the process of coagulation and of the adsorption phenomena accompanying them will decide the question of the heterogeneity of colloids in their normal condition. J. C. S.

Hydrophobe and hydrophile sulfur sols. H. FREUNDLICH AND P. SCHOLZ. *Kolloid-chem. Beihfte* 16, 234-66(1922).—A hydrophile (lyophile) S sol. (A) was prepd. in a chem. way from SO_2 and H_2S with addition of acid to decompose the thiosulfate (Oden). A hydrophobe (lyophobe) S sol (B) was prepd by gradual addition of an alc. S soln. to a large excess of H_2O (Weimarn). Comparative studies of these two types of sols were made. B sol was found electronegative, coagulable by electrolytes, able to adsorb strongly cations especially H^+ , but only very slightly coagulable by OH^- . The sol could only be prepd. in rather small concns., was not reprecipitable and remained stable for a few days only. The differences in properties between A and B are: (1) the alkali salts are 10 to 20 times weaker coagulants of A than of B; (2) the lyotropic series

of the cations is pronounced from weakest to strongest: Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ ; (3) the acids coagulate to a less extent than the alkali salts; (4) alkalis transform **A** to **B**. These differences cannot be explained by the sole assumption that **B** consists of S_λ and **A** of S_μ but that in addition to this distinction **A** contains pentathionic acid while **B** contains none. The acid is difficultly washed free from the **S** and must, therefore, be adsorbed, one g. **S** holding adsorbed 0.1 to 0.7 mole pentathionic acid. The acid has a definite influence on the stability of **A** because the latter is related constitutionally to H_2O as well as to **S** and, therefore, appears as micellae consisting of **S**, pentathionic acid and H_2O . The large amt. of H_2O bound by **A** is further evident on comparing the two sols of the same **S** content, for it is far more transparent than **B**. The structures of the micellae of the two types of sols are further demonstrated by the following facts: (1) alkalis affect the pentathionic acid equil. and thereby the loose combination between **S** and H_2O so that the **A** micellae become **B** in character; (2) acids flocculate **A** very little because they increase the stability of the pentathionic acid and simultaneously increase the quantity of that acid from the available pentathionates; and (3) the lyotropic behavior of the alkali salts may be explained as due to the differences in hydration capacities of the alkali cations, affecting the H_2O content according to their affinity therefor. H_2S acts on **A** as alkalis do, by transforming it to **B** with less stable properties since **S** is set free by decompn. of pentathionic acid by H_2S . **A** may be prepd. in addition to Oden's method by the decompn. of S_2Cl_2 by H_2O according to the equation: $5\text{S}_2\text{Cl}_2 + 6\text{H}_2\text{O} = 5\text{S} + \text{H}_2\text{S}_5\text{O}_4 + 10\text{HCl}$. The stability of Oden's lyophile sol **A** largely detd. by the pentathionic acid is not a function of the charge on the micellae. On addition of NH_4OH the charge remains unaltered or even increases as cataphoresis expts. showed, but alkalis convert **A** to the less stable **B** in which the **S** particles coalesce in rather short time. It could not be definitely demonstrated that the Oden sol contains S_μ but apart from other considerations its yellow coloration compared with the white of Weimarn's sol makes that fact quite evident. The possibility is considered that Alex. Smith's hypothesis that the transition from S_μ to S_λ is effected catalytically, is confirmed in these expts. with pentathionic acid, formed in such systems by the action of water on **S**, serving as catalyst. Alkalis and H_2S accelerate this transition while SO_2 and other acids retard it.

I. NEWTON KUGELMASS

Coagulation by electrolyte mixtures. H. FREUNDLICH AND P. SCHOLZ. *Kolloid-chem. Beihfte* 16, 267-84 (1922).—Oden's results showing that **S** sols may be coagulated by one electrolyte and reprecipitated by another was confirmed but I^+ and **S** show, contrary to Oden, that this behavior is not due to anionic effects on cations but rather to a definite antagonism between cations. This *antagonistic salt effect* was measured by adding to the *lyophile S sol* a quantity of electrolyte insufficient to coagulate it and then detg. the quantity of a second electrolyte necessary to produce coagulation. Pairs of ions with strong antagonism as $\text{Mg}^{++}\text{-Li}^+$ or $\text{Mg}^{++}\text{-H}^+$ showed that the coagulation value of Mg^{++} was much greater than when Mg^{++} alone produced coagulation. Anions play a secondary role and may be arranged in a series: citrate $^-$ ion $>$ SO_4^{--} $>$ Cl^- . Distinct *hydrophobe sols* such as Weimarn's **S** and Donau's **Au** sols showed no such ion-antagonism phenomena on coagulation. The coagulation values in sols contg. electrolytes were less than in aq. sols alone, i. e., the effects of cations were additive as expected from the adsorption theory of coagulation of hydrophobe sols. Furthermore the coagulated sols could not be peptized by electrolytes. It seems most probable that Oden's **S** sol behaves differently because of its hydrophilic character, i. e., with its hydrated micellae. That such is the case is evident from the ions herein involved which are characteristic for their hydration capacities: Li^+ , Mg^{++} , etc. Unlike the hydrophobe **S** and **Au** sols there appeared a definite antagonism for pairs of salts such as LiCl and MgCl_2 in the coagulation of As_2S_3 sols, inasmuch as higher concns. were necessary to

produce coagulation with these electrolyte mixts. than with single salts. This may also be explained on the basis of hydration. Antagonistic salts thus offer a suitable method of detg. the existence and *degree of hydration of sols* and its quant. relation to the degree of stability. These results on ion-antagonism parallel those of Loeb and others observed in biological systems as well as the work of Neuschloss, who showed that with changes in surface tension of a lecithin sol corresponding changes in ion-antagonism were observed.

I. NEWTON KUGELMASS

Sensitization of coagulation processes: Colloids as indicators of photoelectric effects. N. P. PRSKOV. *Bull. Inst. Polyt. Ivanovo-Voznesensk.* 6, 101-4(1922).—Anthracene exerts a sensitizing action on the coagulation of sols of As_2S_3 , Pt, and C, but it is not known if this action is exercised towards all sols or if it is limited to those carrying a definite charge. The action does not depend on chem. transformation of the anthracene nor on its fluorescence, but lies in the electronic transpositions taking place in the system under the influence of insolation. Hence colloids constitute a new type of indicator for photoelectric effects. Reference is made to the various possible interpretations of the mechanism of the coagulation of colloids under the sensitizing action of anthracene.

J. C. SE

The hydrolytic decomposition of glutins and glue testing methods. O. GERNGROSS AND H. A. BRECHT. *Collegium* 1922, 262-81.—The weak acid decompn. of a 25% gelatin soln. of p_H 4.7 at 100° and the very weak alk. decompn. of p_H 7.3 at 55° and at 100° have been studied. The value of p_H remained const. in the acid hydrolysis for 24 hrs., and in the alk. hydrolysis the value of p_H rose slightly and then declined. High temp. furthers the decompn. but harms the viscosity and jelly strength. Alk. hydrolysis affects both properties more than acid. The adhesive power of a gelatin rises as decompn. progresses, reaches a max. and then declines. In acid hydrolysis this decline is const. while in alk. decompn. after a certain length of time it commences to rise again. There is apparently no direct connection between decompn. and viscosity on one hand, and jelly strength and adhesive power on the other. The viscosity and jelly strength of gelatin in the neighborhood of isoelec. points are much smaller than those in the neighborhood of neutral points, while the adhesive power appears to be even higher at isoelec. points than at neutral points.

C. T. WHITE

Rigidity of gels—influence of a dissolved crystalloid. F. MICHAUD. *Compt. rend.* 175, 1196-8(1922); cf. *C. A.* 16, 3242.—Acids and bases diminish greatly the modulus of rigidity of gels of gelose and gelatin, the effect of concd. acids being greater than that of concd. bases. In dil. gels the reverse holds. For gelatin the acid effect on the rigidity is approx. a linear function of the H-ion concn. while the alk. action is a parabolic function of the OH-ion concn. For gelose the action of the base is linear while that of the acid is parabolic. Interpretation of these behaviors is developed on the basis of Jacques Loeb's work on the stoichiometric relations of amphoteric proteins. Salts which hydrolyze behave as acids or bases, as expected, while salts non-hydrolyzed decrease the rigidity about a tenth of that effected by hydrolyzed salts. Org. substances behave variably. Sucrose, dextrose, levulose, mannitol, and glycerol have practically no effect on the rigidity of gelatin or gelose gels. Urea, urethan and acetamide behave like inorg. salts. Resorcinol, hydroquinone, and tannin decrease the rigidity to a greater extent than acids or bases.

I. NEWTON KUGELMASS

Studies in plant colloids. XIV. Physicochemical analysis of agar gels. M. SAMEC AND V. ISAJEVIC. *Kolloidchem. Beihefte* 16, 285-300(1922).—Agar-agar contains considerable quantities of electrolytes bound with sufficient force to be inseparable by dialysis or electrodialysis. The essential constituent of the agar ash indicates the presence of H_2SO_4 , K, and small amts. of silicic acid. The H_2SO_4 can be dialyzed from the agar on boiling the agar soln. under pressure. This loss of S content of the agar

causes a series of physicochem. changes associated with gel formation. Gelose-sulfuric acid in which H_2SO_4 probably appears in ester form was identified as a monobasic acid containing an atom of S per mol. This is the typical constituent of agar-agar whose average mol. wt. has been calcd. to be 9000. Viscosity detns. on the agar gel show a max. at neutrality.

I. NEWTON KUGELMASS

General method for obtaining gels of inorganic salts, and its relation to theories of the colloidal state. K. CHARICHKOV. *J. Russ. Phys. Chem. Soc.* 52, 91-6 (1920).—Treatment of a soln. of Na (K, etc.) naphthenate in a hydrocarbon contg. excess of naphthenic acid with HCl or CO_2 yields colloidal NaCl or Na_2CO_3 . With heavy metal salts of naphthenic acid, which dissolve readily in benzene, toluene, or light petroleum, excess of naphthenic acid is not required; colloidal CuCl_2 and HgCl_2 , etc., are obtainable in this way. The naphthenic acid may be replaced by oleic acid. The products formed show Brownian movement and the corresponding ultramicroscopic appearance. The sol first formed rapidly undergoes coagulation but not throughout its entire mass, part remaining in a condition of pseudo-soln. detectable ultramicroscopically. Treatment of FeSO_4 in the above way results in the formation of a white ppt. which, as oxidation proceeds, is gradually converted first into a black sol of triferrous tetroxide and ultimately into a brown sol of Fe_2O_3 . The action of HCl on ferric naphthenate yields, not FeCl_3 but FeCl_2 , the HCl acting as a reducing agent under these conditions. These and allied phenomena do not appear to be explicable by any of the existing theories of the colloidal state, or by von Weimarn's crystn. theory, which is generally accepted. Neither C.'s formula for expressing the course of sepn. of ppts. nor that given by Nernst to indicate the velocity with which a ppt. forms round centers of crystn. takes into account the attraction or affinity between solvent and solute, which constitutes an important factor; in many cases, the whole process of crystn. is the resultant of the force uniting the mols. and the affinity of the latter for the solvent. C. regards gels and sols as the extreme and final stages of the interactions between solid and liquid phases, intermediate stages being represented by crystals of various degrees of symmetry.

J. C. S.

Topochemical reactions: Formation of crystals in colloidal metals. V. KOHL-SCHÜTTER AND K. STRECK. *Z. Elektrochem.* 28, 554-68 (1922).—The appearance of crystals of Ag in colloidal Ag solns. has been explained, heretofore, partly on a thermodynamic basis as the result of differences in soly. of particles of different sizes, and partly on the ground of direct aggregate-crystn. of ultramicroscopic crystals in consequence of a "mol.-field." Both of these explanations are open to doubt; on the one hand, on account of the extremely small soly. of metallic Ag, and on the other, on account of the surface condition of colloidal particles. It is more probable that the appearance of Ag crystals in colloidal solns. of Ag may result from chem. reactions. Expts. show that during a period of 18 months distinct crystals form in Lea sols; while in pure sols, prep'd. by the reduction of Ag_2O with H, crystals are only deposited in a 12-year-old soln. In the same period visible crystals appeared in gels kept under H_2O , which were free from electrolytes and protecting colloids. Well developed polyhedrons result from the action of Fe^{+++} or Ag^+ ions on coagulated gels. Cryst. forms also develop within a certain concn. range by the reduction of Ag^+ solns. with Fe^{++} . Localization of the same reaction by the use of solid ferrous compds. in Ag^+ solns. and solid Ag compds. in Fe^{++} solns. promotes crystal formation. According to this, crystal formation in colloidal solns. is the result of a ripening process, owing to a movement of the Ag of the micella in the reversible reactions, $\text{Ag} + \text{Fe}^{+++} \rightleftharpoons \text{Ag}^+ + \text{Fe}^{++}$ and $\text{Ag} + \text{Ag}^+ \rightleftharpoons \text{Ag}_2^+$, whereby at the topochem. moment the spatial crowding together of the reaction components and the colloidal particles det's. the sp. form of the cryst. Ag. Observations with different oxides and sulfides suggest that e. m. f. effects

participate in the formation of crystals in colloidal systems. The paper contains a no. of photomicrographs.

H. JERMAIN CRIGHTON

Winkelblech's phenomenon or pseudoextraction and its importance in colloidal chemistry. New methods of extracting solids. K. CHARICHKOV. *J. Russ. Phys. Chem. Soc.* 52, 96-107(1920).—Winkelblech (*C. A.* 1, 680) found that when certain pseudo sols. are treated with various non-aq. solvents insol. in water, the solid disperse phase passes partly or completely into the liquid, non-aq. phase, throughout which it becomes distributed in the form of a gel. This phenomenon is usually regarded as a special case of adsorption, but the results obtained on examg. different combinations of disperse phases and non-aq. solvents are completely incompatible with this view. The effect seems to be due rather to mech. seizure of the mols. of the solid phase by disintegrated liquid drops of lower sp. gr. or to attraction of these mols. to the bottom by mols. of a heavier liquid. From a pseudo soln. of gelatin part of the sol may be drawn to either the surface or the bottom of the liquid by treatment with light petroleum, CHCl_3 , CS_2 , etc., and owing to the resemblance of the phenomenon to extn. C. terms is "pseudo extn." For the velocity of transport of the mols., Lewis's formula, $V = 2r^2S(S - S_1)/9\eta$, should be valid, S and S_1 being the sp. gravities of the solid and liquid phases, r the radius of the mols., and η the coeff. of viscosity, but greater exactitude would be attained by addn. of the term, $2r^2S(S - d)/9\eta$, d denoting the sp. gr. of air. The fact that sols of silicic acid, Prussian blue, and almost all metals remain unchanged when heated with light petroleum, benzene, and similar liquids is explained on the assumption that, for certain values of S and S_1 the magnitude of V will be negative, the specifically lighter mols. of air and light petroleum being then not in a condition to draw upwards the heavier mols. of the sols of metals and various oxides. The results of expts. on the pseudo extn. of gelatin, agar-agar, and Na oleate show that the quantity of the colloidal substance thus extd. is not proportional to the concn.; when the latter is very high, no pseudo extn. takes place. For every disperse phase, the phenomenon appears to exhibit an optimum concn. and an optimum temp. In no case, however, is it possible to remove by pseudo extn. the whole amt. of a sol occurring in the disperse phase. The excess above the normal proportion of K H tartrate or Na_2SO_4 present in supersatd. soln. is withdrawn instantaneously from the latter by shaking with light petroleum. The same occurs when an aq. alc. soln. of sucrose is similarly treated, but in this instance the sucrose withdrawn partly redissolves in the aq. alc. layer on prolonged keeping of the system after being shaken with the light petroleum. J. C. S.

The nature of swelling processes. VI. Swelling and distribution of acetylcellulose in organic media. (After expts. by J. Hogrefe and F. Mertens.) E. KNÖVVENAGEL. *Kolloidchem. Beihefte* 16, 180-214(1922); cf. *C. A.* 15, 2373.—Systems of acetylcellulose in binary mixts. of water, Me, Et and iso-Pr aces., AcMe, glacial AcOH, C_2H_6 , CHCl_3 , camphor, and nitrobenzene were studied to det. by swelling measurements the quantities of liquid bound and those replaceable by others. Definite quantities of single solvents were taken up by acetylcellulose. This is interpreted on the basis of stoichiometry with none but chem. reactions proceeding in such systems. I. N. K.

Researches on electrical colloid syntheses. SVEN BODFORSS and PER FROLICH. *Kolloidchem. Beihefte* 16, 301-40(1922).—Svedberg's colloid syntheses were investigated by means of a high-tension sym. a. c. instead of an induced current. First-approximation relations of degree of dispersion to the length of oscillatory orbit are developed. The capacity for dispersion of the different metals is quant. compared. In general the yield of dispersed metal in mg. per min. is a straight-line function of the applied amperage squared. This confirms the modified form of condensation discharge of sym. a. c. as more effective than induced currents. Binary alloys were similarly studied. The static characteristics of high-frequency a. c. arcs were detd. for Cu, Mg, Al and Ag.

The behavior of arcs in liquids in general is discussed. Metallic dispersion was further studied at various tensions and frequencies.

I. NEWTON KUGELMASS

Changes in volume and refractive index associated with (a) the formation of organosols and gels (b) reversible sol-to-gel transition. E. W. J. MARDLES. *Trans. Faraday Soc.* 1923 (advance proof); cf. *C. A.* 17, 909(1922).—The ds. of the sols were detd. by means of suitable pycnometers and d. hottles. The d. of the cellulose acetate was detd. by allowing a sol of the ordinary white powder to evap. in a flat dish enclosed in a desiccator. The resulting film was kept at 95° until const. wt. was attained. In henzy alc. and petroleum spirit $d_{25} = 1.317$, and $d_{20} = 1.310$. The ds. of rosin and of shellac were obtained similarly, with boiled distd. H_2O as the liquid. Tables of data are given for d. changes in the systems: cellulose acetate in cyclohexane, in acetone, in henzy alc., in triacetin, and in Me acetate; colophony in C_6H_6 , in acetone, in Et and henzy alcs.; and orange shellac in Et and henzy alcs. The greatest vol. change observed was with the system cellulose acetate in acetone when there was a contraction of 0.15% for each g. present. The vol. change is greatest and the colloidal soln. nearest in character to a true soln. when: (1) the concns. are low, (2) the temps. are high, and (3) the best solvent is used. Tables of data for change of n for cellulose acetate in acetone, in cyclohexanone, and in henzy alc. are given. Deductions similar to those for d. change, could be drawn from the data on change of n . Several tables of data show that there are small vol. changes at a reversible sol to gel transition. There seems to be a corresponding change in n .

F. E. BROWN

Reversible sol-to-gel transition in non-aq. systems. I. Change of viscosity with time during gelation. II. Viscosity changes associated with the gel-to-sol transition. E. W. J. MARDLES. *Trans. Faraday Soc.* 1923 (advance proof); cf. *C. A.* 17, 909.—Three types of viscosimeter were used, the Ostwald, the revolving-disk or cylinder and the falling-ball or stream-line plunger. With the Ostwald type change of size of the capillary changed the observed viscosity. The rotation type of viscosimeter gave irregular results especially as the viscosity became high. The falling of a sphere became irregular as viscosity increased. The sphere acted as though it was encountering invisible clots tied loosely to each other, until finally in the more concd. systems the attachments became strong enough entirely to stop its motion. What is measured is not true viscosity but something closely related to it. The system is heterogeneous and mechanical agitation of systems of low concn. destroy the gel structure by breaking the connection between the clots. The change of apparent viscosity with time, during the gelation of a sol of cellulose acetate can be expressed by the empirical formula $\eta - \eta_0 = ae^{kt}$ where η is the apparent viscosity after an interval of time t , η_0 is the original viscosity, k the rate of gelation, and " a " depends on η_0 and k . The temp. where k becomes nil is the *max. gelation temp.* The relation between this temp. and concn. resembles that between temp. and satn. pt. for crystalloids. Twenty tables of data and 7 graphs are given to show the relation of viscosity to time, during gelation. When a gel is warmed above the temp. of zero fluidity, the viscosity changes might be represented by a curve which is approx. a mirror image of the gelation curve. Rate of solution is a function of temp. and time, and is promoted by mechanical action. The viscosity of the original sol is attained without mechanical action at a temp. known as the *minimum solution temp.*, but not below it. The age and thermal history of the gel exert considerable influence on its solution. For one gel, the time of solution was more than doubled by standing overnight. The minimum solution temp. is about 16° above the *max. gelation temp.* Eight extensive tables of data are given in the part of the paper dealing with solution.

F. E. BROWN

The solution of tetramethylammonium aluminate. JINDRICH BREZINA. *Chem. Listy* [2] 16, 25-6(1922).—Metallic Al is dissolved in a soln. of $N(Me)_4OH$, and the

cond. of the soln. with varying amts. of Al is measured. From the measurements thus obtained it is deduced that the $\text{Al}(\text{OH})_3$ produced is neutralized in the same way as by an inorg. base, and that it acts as a monobasic acid, since soln. of Al ceases when there is present 1 mol. of $\text{Al}(\text{OH})_3$ to one of base. The salt thus formed is highly dissociated in soln. The transport no. for the anion of orthoaluminic acid is 24 at 0° . J. C. S.

Behavior of sulfides of heavy metals in aqueous solutions. O. WEIGEL. *Sitzb. Ges. Naturw.* Marburg, 1921, No. 2, 35-50; cf. *C. A.* 1, 1217.—The known solubilities of heavy metal sulfides as experimentally detd. are generally greatly in excess of the values calcd. from their soly. products. W.'s detns. of the solubilities of the sulfides of Tl, Ag and Pb show that in each case the calcd. soly. is less than that detd. experimentally. From the effect of Pb ions on the soly. of PbS and the potential of a PbS electrode, it is concluded that dissoc. in aq. soln. takes place in successive stages and that most of the dissolved substance is in the form of complex ions. Removal of metallic ions by addn. of sulfide ions depends on the formation of complex ions. J. C. S.

Solubility of Berlin blue. MORITZ KOHN. *Monatsh.* 43, 373-6 (1923).—Berlin blue is sol. in neutral oxalates of K, Na and NH₄ with a green color. This soly. is not materially influenced by the presence of FeCl_3 or $\text{K}_4\text{Fe}(\text{CN})_6$. In contrast with the previously known colloidal deep-blue solns. of Berlin blue in $(\text{CO}_2\text{H})_2$, the solns. in the neutral oxalates show all the properties of true solus. The proof of Fe^{+++} by means of the Berlin blue test therefore loses its reliability in the presence of neutral oxalates.

C. J. WEST

Thermal expansion of concentrated salt solutions. ROBERT MEYER. *Physik. Ber.* 3, 149 (1922).—The thermal expansions of aq. solns. of NaNO_3 , KNO_3 , ZnSO_4 and K_2CO_3 , satd. at $20-70^\circ$, were measured at temps. up to 90° . The coeff. of expansion of concd. solns. increases with rise of temp., but while in the case of water the rate of increase of the coeff. of expansion decreases smoothly with rise of temp., the curves obtained for concd. salt solns. are irregular and show points of inflection the positions of which depend on the concn. of the soln. J. C. S.

Theory of solvates. JA. K. SYRKIN. *Bull. Inst. Polyt. Ivanovo-Voznesensk* 6, 267-80 (1922).—Solvates in general and hydrates in particular vary in compn. and are stable only within narrow limiting conditions, so that they must be regarded as transitory systems of physicochem. character. The structure of a hydrate may be represented as a mol. of solute surrounded by an envelope of water mols. Such of the latter as are near to the nucleus are held by a force approximating to chem. force, whereas the more remote, semi-combined water mols. exist under the configurational influences of chem. and kinetic forces, the system being in a condition of stationary thermal equil. Hence it is possible for hydrates of different compn. to exist in one and the same soln. This equil. of hydrates possesses a macroscopic character. The gradual variation of the thermal effect with the temp. confirms these views and distinguishes the decompn. of a hydrate from the stoichiometric decompn. of an ordinary system. The existence of hydration is shown also by the change in the internal pressure, and the work of the internal forces may be expressed as the mech. equiv. of chem. affinity (cf. TAMMANG, "Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen" 1907, 34). J. C. S.

Hydrolysis of methyl *o*-nitrobenzoate in acid solution. G. E. K. BRANCH AND D. S. MCKITTRICK. *J. Am. Chem. Soc.* 45, 321-7 (1923).—The rates and equil. of the hydrolysis of Me *o*-nitrobenzoate (*a*) and Me benzoate (*b*) and the esterification of *o*-nitrobenzoic acid (*c*) were studied at 133° under the same conditions. It was found that (1) the equil. for (*a*) and (*b*) were practically the same; (2) the esterification of (*c*) was of a higher order than the corresponding hydrolysis; (3) the rate of hydrolysis of the nitrobenzoic ester was 0.05 as great as that of the benzoic ester. H. J. C.

Kinetics of inductive processes: Schönbein's reaction. A. V. PAMFILOV AND N. N. PETIN. *Bull. Inst. Polyt. Ivanovo-Voznesensk* 6, 221-31(1922).—The authors discuss previous work on the influence of FeO on the liberation of I from an iodide by the action of H_2O_2 , and give the results of their own expts. on this reaction. Not only the velocity of the initial stage of the reaction, but also the nature of its dependence on the concn. of the iron salt and on the corresponding acidity are completely different according as the iron is in the ferric or the ferrous condition. The liberation of I by Fe_2O_3 or H_2O_2 separately is considerably accelerated when the two reactions occur together, and the velocities of the sep., and that of the combined, reactions increase with increase of the concns. of all the components; the acidity of the medium is of comparatively little influence, but in general accelerates the reaction. On the other hand, in neutral and faintly acid media the reaction is accelerated more by FeO than by Fe_2O_3 in low concn., but for definite conditions of concn. the reaction is retarded by increasing the concn. of the FeO either absolutely or in relation to the KI; this retardation is observed also in an acid medium. Increase in the acidity also retards the reaction considerably. This phenomenon disappears when the concn. of the KI increases and the soln. is rendered strongly acid, especially as liberation of I by the acid becomes pronounced under these conditions. Hence the diminution in the sensitiveness of Schönbein's reaction in a neutral medium caused by increase in the concn. of the catalyst (cf. Meissner, "Untersuchungen über den Sauerstoff," 1868, 78-80; Struve, *Z. anal. Chem.* 8, 319(1869)) is not fortuitous but holds generally, both in acid and in neutral solns. The results of replacement of the acid by the corresponding concn. of a sulfate show, as was found by Brode [*Z. physik. chem.* 37, 257-307(1901)] for ferric ions, that the influence of increased acidity is not to be referred to diminished concn. of the ferrous ions and that the H ions must here play a part. The mechanism of the action of FeO, typical of inductors in general, is probably based on its spontaneous oxidation, and the retarding influence exerted on the reaction by acidity is related to the great stability of ferrous ions in an acid soln. J. C. S.

Equilibrium in heterogeneous systems. JA. K. SYRKIN. *Bull. Inst. Polyt. Ivanovo-Voznesensk* 4, 161-5(1921).—Investigation of the reaction $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$ with concns. ranging from 0.01 to 0.002 g. inol. per l. and thus corresponding with widely varying degrees of dissociation of the component salts, shows that the reaction does not conform to the law of equilibrium, the "constants" of the reaction exhibiting wide divergences. The reaction is reversible, the reversibility, that is, the proportion of non-reacting mols., amounting to 58% at the ordinary temp. and at low concns. At 7° scarcely any action occurs. The value of the reversibility at 38° is similar to that at 18°, probably owing to the soly. of $CaSO_4$ being at a max. at 38°. The reversibility is a function of the concn. and increases with diln., the more rapidly at low temps. Thus, with reactions involving the formation of a new phase the laws of equilibrium are incomparably more complex than with homogeneous reactions. At present, the dependence of the reversibility on the concn. is expressible only by an empirical relation of the form $Z = 1 + ac + bc^2 \dots$ J. C. S.

Union of hydrogen with acetylene derivatives. XV. Velocities of catalytic reactions. I. S. ZALKIND. *J. Russ. Phys. Chem. Soc.* 52, 199-211(1920); cf. *C. A.* 11, 584.—A discussion of results obtained by various investigators on the course followed by reactions occurring under the influence of enzymes and other catalysts. The general conclusion is that even when catalysts so chemically simple as Pd and Pt are used, the course of the reaction is often quite complex, and that no essential difference exists between the actions of these simple catalysts and those of enzymes. In both cases, it is necessary to assume the formation of intermediate compounds between the catalyst and the reacting compounds, although with regard to the means by which such intermediate

comps. are formed—whether by chem. reaction or by simple adsorption—opinions differ. Adsorption phenomena may, indeed, exhibit complex character and a sharp distinction between adsorptive and chem. phenomena is scarcely possible. J. C. S.

Studies of oxidation catalysis. III. L. KARCZAG. *Biochem. Z.* 132, 270-8 (1922); cf. *C. A.* 15, 3781.—Dil. solns. of 94 dyestuffs were tested as to their decolorization by H_2O_2 . The comps. could be sepd. into a decolorizable and a non-decolorizable group as distinct from the action of H_2O_2 in the presence of metallic salts when all dyestuffs are decolorized. The reaction is considered as an intramol. change in the color-producing radical. The dyestuffs which are decolorized belong almost without exception to the triphenylmethane series. However, only those members of this series which have the benzene radical free or combined together through a C atom are attacked. A ring union between 2 benzene rings leads to resistance to decolorization. On the other hand derivs. of fluorescein and eosin are resistant. The azo dyes, pyrazolone dyes, benzidine dyes and the nitro dyes also are resistant. The condensation of the benzene ring contributes to resistivity as shown by the relatively higher stability of the anthracene dyes. Among the heterocyclic (tricyclic) comps. those which contain O, or an O and a N atom in the central ring are decolorizable as are the derivs. of the pyroline and oxazine. Those dyes of the same type which have N, 2 N's, or an N and a S atom are resistant; e. g., the derivs. of quinoline, acridine, phenazine and phenothiazine. The decolorization of the triphenylmethane dyes by H_2O_2 is a more deep-seated change than that caused by NaOH. The velocity of the decolorization by H_2O_2 is accelerated by alkali and retarded by acid. The catalyzing action of alkali is due to the blunting of the inhibiting action of the acid of H_2O_2 soln. as shown by expts. in which neutral H_2O_2 solns. were used. The changes in the presence of NaOH and H_2O_2 are of the same general nature as when H_2O_2 alone is used, but certain dyes are attacked which are resistant to H_2O_2 alone. The dyes altered by NaOH are capable of regeneration after 24 hrs. Those changed by H_2O_2 alone are completely capable of regeneration immediately after the reaction, but incompletely after 24 hrs. and with different intensities. The decolorization by NaOH + H_2O_2 is of the H_2O_2 type and not of the NaOH type. The presence of NaOH provides a certain protection to certain dyes against the secondary influence of H_2O_2 . Regeneration studies with acid, wool, cotton and silk demonstrate that the action of H_2O_2 on the triphenylmethane dyes is mainly a rearrangement; along with this secondary reactions occur which induce deep-seated changes in the dye like the analogous reactions caused by NaOH. F. S. HAMMETT

Application of thermodynamics to heterogeneous equilibria. G. W. MORRY. *J. Franklin Inst.* 194, 764(1922).—Corrections to a paper previously noted (*C. A.* 16, 4118).

JOSEPH S. HEPBURN

Gas pressures and the second law of thermodynamics. F. D'E. ATKINSON. *Nature* 110, 112-3(1922).—Polemical against Fairbourn, *C. A.* 16, 2799. Reply. ARTHUR FAIRBOURNE. *Ibid* 113.

C. R. PARK

Thermochemistry of solutions. M. LEVATY-EZERSKY. *J. Russ. Phys. Chem. Soc.* 52, 108-13(1920).—Simple reasoning from fundamental principles leads to a no. of equations which may be combined in the form: $q^1_m = q_m - Bq^1_t = BQ_1 - Q_m = \phi_1 - \phi_m = BR_1 - R_m$, where q^1_m represents the heat of diln. of a soln. contg. 100 $m/(100 - m)$ g. of solute per 100 g. of water to the concn. 1%, and q^1_m and q^1_t have analogous significations; Q_1 and Q_m are the heats of soln. of 100/(100 - l) and 100 $m/(100 - m)$ g., resp., of the solute in 100 g. of water; $\phi_m = Q_m$ and $\phi_1 = m(100 - l) $Q_1/(100 - m)$, that is, $\phi_1 - \phi_m$, corresponds with the difference between the heats of soln. of one and the same quantity of the solute in such different amts. of water that solns. of 1% and $m\%$ concn., resp., are obtained; R_1 and R_m represent, resp., the heats of reaction of 100/(100 - l) and 100 $m/(100 - m)$ g. of the solute, liquefied at the$

temp. of the expt., with 100 g. of water. The above equation furnishes a convenient means of passing from the heats of soln. of different amts. of a substance in one and the same amt. of solvent to the heats of soln. of one and the same quantity of solute in different quantities of solvent and from these to the heats of diln. J. C. S.

Proposal for the fixing of a unit of measurement in thermochemistry. W. SWIEN-ROSLAWSKI. *Roczniki Chemji* 1, 479-87(1921); cf. C. A. 16, 2804.—The following proposals were put forward at the Intern. Chem. Conference at Brussels in 1921. The heat of combustion of 1 g. of benzoic acid, in cal. at 15°, should be taken as the unit, rather than that of cane-sugar, which is hygroscopic, or of naphthalene, which is liable to sublime. By using one substance only for the standard, many const. calorimetric corrections would not be needed, and a simpler formula could be used. Certain discrepancies in the values for the heat of combustion of benzoic acid, as obtained by various workers, are pointed out, and also in the ratios for the heats of combustion of benzoic acid, cane-sugar, and naphthalene. It is proposed that the heat of combustion of benzoic acid at const. vol. be taken provisionally as 6321 cal. until it may be more accurately redetd. by the method of adiabatic measurement. J. C. S.

* **Approximate rule for the specific heats of gases and vapors.** RUDOLF MEWES. *Z. Sauerstoff Stickstoff Ind.* 14, 26(1922).—From the formulas $cp = cp_0(1 + \gamma)^1$ and $cp/cp_0 = (c'p/c'p_0)^n$ the sp. heat of a substance can be calcd. for all temps. Values are given of $\log(1 + \gamma)$ and n , resp., for a no. of gases and vapors. The values of $\log(1 + \gamma)$ are simple multiples of each other, while the values of n are simple integers. J. C. S.

The theory of the specific heat of liquids. K. HONDA. *Phil. Mag.* 45, 189-92 (1923).—A new theory of the sp. heat of liquids is based on the consideration of the *phenomenon of melting* from the standpoint of the *space lattice of crystals*. A substance monatomic in the solid state and undergoing no change in association upon melting is considered. An atom in the space lattice has 3 degrees of vibratory freedom and small dependent rotational vibrations. On approaching the m. p. the amplitude of the rotational vibrations increases until, at the m. p., continuous rotation results, spacing breaks down, disorder of the at. arrangement ensues, or melting takes place. On this basic hypothesis a theory is built from which it is deduced that the total energy W of a substance at temp. T above its m. p. T_m is: $W = 3RT_m + (nRT/2) + Q + 3R(T - T_m)(1 - e)$ where n is the no. of degrees of freedom, Q is the small external work involved by the change of vol. at the m. p., R is the gas const. and e is a no. between 0 and $1/2$. The at. heat at const. vol. in the liquid phase is: $C_v = dW/dT = 3R(1 - e) + (nR/2)$. Hence C_v lies within the following ranges: for $n = 2$; 4.95 to 7.92; for $n = 3$; 5.94 to 8.91. If C'_s is the at. heat in the solid state at the m. p., $C_v - C'_s = R[(n/2) - 3e]$, which is the change in the at. heat during melting and may have a positive or a negative sign according to the nature of the substance. S. C. LIND

Heats of vaporization. W. HERZ. *Z. anorg. allgem. Chem.* 124, 56-8(1922).—The ratio between the heats of vaporization at $2/3$ and $1/4$ of their crit. temps. for 25 liquids is nearly const., 1.4. The data of Young (C. A. 5, 406) were used for the following liquids: pentane, hexane, heptane, octane, isopentane, diisopropyl, diisobutyl, hexamethylene, benzene, fluorobenzene, chlorobenzene, MeOH, EtOH, PrOH, CCl₄, SnCl₄, Et₂O, HCO₂Me, HCO₂Pr, AcOH, Me propionate, Pr acetate and Et propionate. Except for the associated liquids MeOH, EtOH, PrOH and AcOH, the quotient L/T for the above liquids and for a few others closely related is a linear function of T nearly up to the crit. point. JAMES M. BELL

Thermal analysis of the system *o*-*p*-toluenesulfonamides. A. F. DOBRIANSKI. *J. Russ. Phys. Chem. Soc.* 52, 139-44(1920).—Thermal analysis of this system yields a m. p. curve composed of two branches intersecting at the eutectic point about 108°.

which corresponds with 42.5% and 57.5% of the *o*- and *p*-isomerides, resp. This eutectic point is identical with the m. p. of the non-separable mixt. of the two amides obtained in practice when the mixt. of the corresponding *o*- and *p*-chlorides is treated with NH_3 . Sepn. of the *p*-amide from this mixt. by fractional pptn. should hence be, and is found experimentally to be, impossible. The acicular crystals, m. 120° , mentioned by Fahlberg, correspond with a mixt. in equal parts of the two isomerides, but no indication is obtained of the formation of a mol. compd. and no distectic point is observed; such crystals are readily resolved into their components under the microscope.

J. C. S.

System $\text{Na}_2\text{O}-\text{CO}_2-\text{NaCl}-\text{H}_2\text{O}$, considered as two four-component systems. F. A. FREETH. *Trans. Royal Soc. (London)* 223A, 35-87(1922).—The soly. relations in the systems $\text{Na}_2\text{CO}_3 - \text{NaCl} - \text{H}_2\text{O}$; $\text{Na}_2\text{CO}_3 - \text{NaOH} - \text{H}_2\text{O}$; $\text{Na}_2\text{CO}_3 - \text{NaHCO}_3 - \text{H}_2\text{O}$; $\text{NaOH} - \text{NaCl} - \text{H}_2\text{O}$; $\text{NaHCO}_3 - \text{NaCl} - \text{H}_2\text{O}$; $\text{Na}_2\text{CO}_3 - \text{NaOH} - \text{NaCl} - \text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 - \text{NaHCO}_3 - \text{NaCl} - \text{H}_2\text{O}$ have been experimentally detd. at 0° , 10° , 15° , 20° , 25° , 30° , 35° , 45° , and 60° . Numerous tables of the results and diagrams representing the relationships are included in the paper, from which the compn. and quantity of the stable phases formed from any mixt. of the components may be deduced.

J. C. S.

The system $\text{Bi}_2\text{O}_3-\text{PbO}$. L. BELLADEN. *Gazz. chim. ital.* 52, II, 160-4(1922).—The series of minerals consisting of double sulfides of Bi and Pb may be considered as derived from hypothetical ortho-, meta-, and pyrothiobismuthic acids. B. detd. the fusion diagram of the system $\text{Bi}_2\text{O}_3-\text{PbO}$ in order to det. if the S can be replaced with O in these acids. The various mixts. (30 g.) were fused in an elec. furnace and temps. detd. with a Pt-PtRh thermocouple. Litharge and Bi_2O_3 obtained by calcination of $\text{Bi}(\text{NO}_3)_3$ in a muffle were used. A Pt crucible was used; it was not much attacked below 800° . The cooling curve for mixts. from 66 mol. % to 80 mol. % Bi_2O_3 shows 2 arrests at 695° and 680° , resp. The arrest at 695° evidently corresponds to the formation of a definite compd. decomposable on melting. The duration of the 1st arrest is greatest at 80 mol. % Bi_2O_3 while the 2nd is not yet appreciable at this compn. From this it is deduced that the compd. corresponds to $4\text{Bi}_2\text{O}_3\cdot\text{PbO}$. The solidification temp. continues to fall to a eutectic point at about 64 mol. % Bi_2O_3 and then rises. A max. occurs at 60 mol. % Bi_2O_3 corresponding to a 2nd compd. $3\text{Bi}_2\text{O}_3\cdot 2\text{PbO}$, contg. 75.78% Bi_2O_3 , that m. 686° . The curve then falls to a eutectic at about 35 mol. % Bi_2O_3 and then rises to a distinct max. at 33.33 mol. % Bi_2O_3 , corresponding to a third compound, $\text{Bi}_2\text{O}_3\cdot 2\text{PbO}$, contg. 50.98% Bi_2O_3 , that m. 625° . At about 26 mol. % Bi_2O_3 there is a 3rd eutectic, after which the curve rises to the f. p. of PbO . The results of the thermal analysis were confirmed and completed by the microscopic examn. For this purpose the mixts. were poured on a porcelain plate and roasted at 500° or 650° . The specimens were so fragile that they were imbedded in Wood's alloy for further examn. Those rich in Bi were etched with 4% HNO_3 , those rich in Pb with 2%. Four photomicrographs are reproduced. Of the 3 compds. found only 2 have a compn. corresponding to the natural double sulfides: $2\text{PbO}\cdot 3\text{Bi}_2\text{S}_3$ and $2\text{PbO}\cdot\text{Bi}_2\text{S}_3$ correspond to $2\text{PbS}\cdot 3\text{Bi}_2\text{S}_3$ and $2\text{PbS}\cdot\text{Bi}_2\text{S}_3$, resp.

E. J. WITZEMANN

Physicochemical equilibrium and the phase rule. B. L. VANZETTI. *Scientia* 27, 275-89(1920).—A general survey of equil. in homogeneous and heterogeneous systems and the development of the phase rule by Gibbs.

C. C. DAVIS

Electrical conductivity in solid crystallized compounds. III. The electrical conductivity of silver sulfide and cuprous sulfide. C. TUBANDY, SOPHIE EGGERT, AND GUSTAV SCHIBBE. *Z. anorg. allgem. Chem.* 117, 1-47(1921).—The methods described in previous papers (*C. A.* 14, 3352; 15, 1850) have been used for the investigation of the

elec. cond. of Ag_2S and Cu_2S , to settle the question whether these are metallic or electrolytic conductors. The conduction of Ag_2S between metallic electrodes is interfered with by the rapid growth of a metallic bridge between the electrodes. This difficulty was overcome, as in previous work, by interposing between the small cylinder of Ag_2S and the Pt cathode a cylinder of AgI , a Ag anode being used. The α -form of Ag_2S , stable above 179° , was found to be a pure electrolytic conductor, following Faraday's law perfectly. The current is carried entirely by the Ag ions with the high migration velocity of 0.11 cm. per sec. The form of Ag_2S , stable below 179° , however, was found to be a mixed conductor, about 80% of the current being carried by the Ag cations, the remainder being conveyed as in a metallic conductor. For the ingenious exptl. method by which this result was obtained, the original must be consulted. The proportion of the current carried electrolytically is influenced to some extent by the presence of impurities in the Ag_2S , by the temp., and by the current strength. The lower limit of temp. for the expts. was 145° , the transition point of AgI , since only the cubic form of this substance is effective in preventing metallic short-circuiting. The proportion of metallic conduction was found to increase with falling temp. and with increasing current strength. Only the high-temp. form of CuI could be investigated, as its transition point, 91° , is below that of AgI . After many exptl. difficulties had been overcome, it was shown that the cubic form of CuI is a pure electrolytic conductor, the current being carried solely by the cupro-ions. IV. The electrical conductivity of solid silver sulfide silver mixtures. C. TUBANDT and SOPHIE EGGERT. *Ibid* 48-58.—When a current is passed through a solid cylinder of a mixt. of Ag sulfide and Ag , using a Ag anode and Pt cathode with a cylinder of AgI between the cathode and the solid electrolyte (cf. above) above 179° , the amt. of Ag dissolved from the anode is not in agreement with Faraday's law, although at this temp. Ag sulfide is a pure electrolytic conductor. It is found, however, that if the electrolysis is continued for a sufficient length of time, the whole of the Ag in the Ag_2S gradually wanders to the cathode, leaving eventually pure Ag_2S , which then behaves as a pure electrolytic conductor. This phenomenon can be utilized to free Ag_2S from Ag , and also provides a method of proving the formation of a Ag bridge when Ag_2S is electrolyzed between metal electrodes. It also verifies the results of other workers that Ag and Ag_2S do not form mixed crystals, but a coarse mech. mixt. The expts. were made with mixts. contg. up to about 13.5% of Ag . J. C. S.

The effect of pressure on the electrical resistance of cobalt, aluminium, nickel, uranium, and cesium. P. W. BRIDGMAN. *Proc. Am. Acad. Arts Sci.* 58, No. 4, 151-61 (1923); cf. *C. A.* 16, 376.—The pressure coeff. of resistance, between 0 and 12000 kg., at several temps., and the temp. coeff. of resistance between 0° and 100° , at atm. pressure, have been redetd. on purer samples of Co , Al , and Ni , as a supplement to former work. These pressure coeffs. are of the order of 10% higher than the previous values. The results verify the observation that in most cases impurity depresses the pressure coeff., but by a less amt. than it does the temp. coeff. The anomaly of the decrease of the temp. coeff. of resistance of Al with increasing purity is shown to disappear in the region beyond 0.1% impurity, and at sufficiently high purities the temp. coeff. increases with increasing purity as it does for all metals. For U the temp. coeff. of resistance, between 0° and 100° , was only 0.00230, indicating that the specimen was not of high purity. The av. pressure coeff., at 30° , between 0 and 12000 kg., was -0.0436 . The resistance therefore decreases under pressure as is normal for most metals. The sp. resistance of this sample of U , at 0° , was 76.0×10^{-6} . This is high for a metal, being of the order of magnitude of the resistance of liquid Hg , or Bi . Cs has a new polymorphic modification at high pressures, of smaller vol. than the ordinary modification. The transition pressure is sharp and varies with the temp. The transition pressure

at 0° is 1980 kg., and at 17°, 3260 kg. Linear extrapolation of the transition line gives —26° as the atmospheric transition temp. The elec. properties of the high-pressure modification are anomalous in that the resistance increases with increasing pressure. It is the 6th metal known with this property. The resistance of the new modification was measured, at 0°, from the transition pressure to 12000 kg. The curve is of the same character as for the 5 other abnormal metals. The av. pressure coeff. between 11000 and 12000 kg. is 0.000493. This is about the same as that of Sr, which has the highest coeff. of the abnormal metals hitherto measured. At the transition point there is a discontinuity in resistance in the normal direction, the high-pressure phase having the smaller resistance. At 0° the resistance of the high-pressure modification at the equil. pressure is 0.407 that of the low-pressure form. The work on Cs is preliminary.

R. H. LOMBARD

Piezoelectric method for the instantaneous measurement of high pressures. J. C. KARCHER. *Bur. Standards, Sci. Papers* No. 445, 257-64(1922).—A number of quartz plates cut from quartz crystals in such a way that their faces are plane, parallel and perpendicular to an elec. axis of the crystal are arranged condenser fashion in a stack and introduced into an elec. circuit. When subjected to a compressional force in the direction of the elec. axis and normal to the faces, a quantity of electricity will be liberated at these faces proportional to the force applied. The quartz plates are subjected to the gas pressure to be measured by means of a piston. The combination of these constitutes a gage which is screwed into the wall of the gas chamber. The leads are brought out through holes drilled through the wall. Readings are made by a ballistic galvanometer, with a period long compared to the duration of the pressure, which is connected to the electrodes of the quartz plates. The galvanometer deflections are photographically recorded on a rapidly moving film. The pressure-time curve is the differential of the recorded deflection-time curve. A diagram showing the assembly of the app. is given.

E. F. PERKINS

Compressibility measurements on solid bodies. E. MADELUNG AND R. FUCHS. *Ann. Physik* 65, 289-309(1921); *Science Abstracts* 24A, 651; cf. preceding abstract.—Recent developments of the crystal lattice theory have necessitated further measurements of the compressibility of crystals having a simple chem. constitution. Previous measurements, which in many cases require verification, are given in tables taken from the papers of Regnault and Amagat for metals, Röntgen and Schneider for rock salt and sylvine, Voigt for characteristic representatives of the crystal systems, Richards and his pupils for numerous elements and the halides of Na, K, Ag, and Th, and Grüneisen for metals. The exptl. methods employed may be classified in two groups: (1) piezometric; (2) detn. from elastic consts. In the present investigation the *piezometric method* was considered with all the variations as used by Voigt, and a new app. designed, which is described in detail and illustrated by several diagrams. The compressibilities and densities of 57 mostly simple minerals are given; they include 40 new detns.

H. G.

The laws of conduction of electricity in super-conductors. H. KAMMELINGH ONNES. *De Ingenieur* 37, 695(1922).—Some of the problems under present investigation, by O. in reference to super-conduction are: to find out the time required for the phenomenon to appear and to disappear; whether the surface of the conductor plays a special role, etc. No exptl. results are given.

R. BEUTNER

Electrolytic valve action. IV. The disintegrating action of the maximum voltage discharge. A. GÜNTHER-SCHULZE. *Z. Physik* 9, 225-45(1922).—When an Al anode is placed in soln. and a const. current value caused to flow the voltage required gradually rises as the thickness of the oxide coat upon the metal surface increases, until a point is reached where an audible discharge takes place through the oxide layer. The

attainment of this max. voltage is accompanied by the liberation of an abnormally large amt. of gas, consisting of H_2 , O_2 and H_2O_2 . The excessive evolution does not take place until this point is reached and continues thereafter as long as the discharge takes place. In case of an Al anode in boric acid with a max. voltage of 1890 the quantity of gas is 10 times that to be expected from electrolysis. The max. voltage depends upon the concn. of the soln., increasing with diln. of the electrolyte. In solns. of boric acid and borax with an Al anode, increase of the max. voltage up to 1150 was accompanied by a small increase in the excess quantity of gas. Further increase in the max. voltage was accompanied by a very rapid increase in excess gas. With rapid changing of the current the excess gas given off is approx. proportional to the square of the current. With slow changing of the current the quantity depends largely upon the cooling of the soln. In concd. solns. of NH_3 , HCO_2H and $AcOH$ $\alpha = b(i - i_0)$ where α is the excess gas, b is a const., i is the current and i_0 the residual current which flows in the ordinary electrolytic way. The relation of the concn. of the above solns. and the quantity of excess gas has been investigated. This investigation has lead to the conclusion that ammonia up to a concn. of 0.4 N is dissolved as NH_4OH and above that as NH_3 .

C. R. PARK

Theory of polarization of electrolytic oxygen evolution. I. Anodic behavior of cobalt in alkali hydroxides. G. GRUBE AND O. FRUCHT. *Z. Elektrochem.* 28, 568-79 (1922).—In concd. solns. of KOH, anodic Co dissolves at high current densities with the formation of a deep blue soln. of K cobaltite: $Co + 2\oplus = Co^{++}$, and $Co^{++} + 4OH^- \rightleftharpoons CoO_2^{--} + 2H_2O$ or $Co^{++} + 3OH^- \rightleftharpoons HCoO_2^- + H_2O$. The results of potential measurements of Co against blue solns. containing different amounts of Co in 8 N KOH show conclusively that the blue compd. is K_2CoO_2 and not colloidal $Co(OH)_2$. From these measurements the value -0.52 v. has been calcd. for the normal potential of Co against K_2CoO_2 . The anodic oxidation of a K_2CoO_2 soln. at Pt takes place in 3 stages: (a) at low potentials Co_2O_4 is formed; (b) at medium potentials Co_2O_3 is produced; (c) at high potentials a solid soln. of CoO_2 in the lower oxides results, oxygen being evolved. The electrolytic evolution of O at Co anodes in alkali hydroxides takes place as follows: the Co unites with the charged at. O with the formation of CoO_2 , and this decomposes into mol. O and Co_2O_3 . II. The anodic behavior of manganese in alkali hydroxides. G. GRUBE AND H. METZGER. *Ibid* 29, 17-30 (1923).—At low current densities anodic Mn dissolves in hot, concd. NaOH with the formation of Mn^{++} ions, while at medium c. d. Mn^{+++} ions and at high c. d. Mn^{++++} ions are produced. The resulting soln. of the manganous oxide is colored yellow-red, that of the manganic oxide brown-red. The hexavalent Mn ions react to form manganate with the evolution of O. At room temp. anodic Mn dissolves in dil. alkali with the formation of permanganate and O is evolved. The potentials corresponding to the different anodic processes have been measured. The results of a systematic study of the polarization of the electrolytic evolution of O in NaOH at Mn anodes show that the anodes become coated with a layer of MnO_2 from which permanganate is formed according to the equation, $MnO_2 + 2H_2O + 3\oplus = MnO_4^- + 4H^+$. At low c. d. the latter decomposes in N NaOH according to the equation, $2HMnO_4 = 2MnO_2 + H_2O + 3/2 O_2$, while at higher c. d. it only partly decomposes. The concurrence of the velocity of the 2 reactions, anodic oxidation of the MnO_2 to $HMnO_4$ and the spontaneous decompn. of the latter with evolution of O, detcs. the extent and the potential with which the current is used for the evolution of O and the formation of permanganate.

H. J. C.

Diffusion of cathodic hydrogen through iron and platinum. M. BODENSTEIN. *Z. Elektrochem.* 28, 617-26 (1922).—Expts. have been carried out on the diffusion of cathodic H through Fe, with the object of finding a relation between the over-voltage

of the cathode and the velocity of diffusion of the gas. Both Tafel's theory of overvoltage (cf. *Z. physik. Chem.* **34**, 199) and that of Möller (cf. *C. A.* **2**, 2489; **3**, 1239) lead to the relation $\log D = a + (e/0.057)$, where D is the velocity of diffusion, e the overvoltage and a is a const. Actually it has been found that $\log D = a + (e/m)$, where $m = 0.1$ to 0.9 , according to the cell employed. From Tafel's theory the relation $D = n\sqrt{I}$ has been deduced, where I is the current strength and n is a const., and this has been verified exptly. H diffuses into Fe in the form of atoms. Attempts to pump at. H from the interior of the cathode and cause it to combine with Br vapor have not been successful. When S is introduced into the cell union with H does not take place; N forms traces of NH_3 and O considerable quantities of H_2O . Expts. in which Cl was passed through the interior of a Pt tube, which served as a cathode, yielded negative results. The results of the investigation indicate that H does not leave the cathode in the form of atoms, but as mols.

H. JERMAIN CREIGHTON

The molecular scattering of light in liquid mixtures. C. V. RAMAN AND K. R. RAMANATHAN. *Phil. Mag.* **45**, 213-24(1923).—The approx. investigation of the scattering of light in liquid mixts. by Einstein (*C. A.* **5**, 1215) is revised and a rigorous formula is developed, in which account is taken of the compressibility of the mixt. The thermodynamical investigation leads to the result that the light scattering arises in 2 distinct ways: (1) due to spontaneous local fluctuations in the compn. of the mixt., and (2) due to local fluctuations of its d. Einstein's treatment ignores the second effect, which becomes very important at temps. not close to the crit. soln. point or in the case of liquids which are completely miscible at ordinary temps. The scattering power is expressed in terms of the compressibility of the mixt., the variations with compn. of its refractive index and of the partial vapor pressures of its constituents. The effects of mol. anisotropy which gives rise to an additional "orientation-scattering" are discussed. The polarization of the transversely scattered light is imperfect as the result of mol. anisotropy, but it is considerably less so in the mixt. than in the pure liquids, and becomes more nearly perfect as the crit. soln. temp. is approached. Comparison of the results with the available exptl. data shows a general agreement. Similar methods may also be applied in the case of solns. of solids in liquids and in the case of ternary mixts.

S. C. LIND

The scattering of X-rays in liquids. C. V. RAMAN. *Nature* **111**, 185(1923).—The X-ray diffraction rings for liquids, ascribed by Keesom and Smedt (*C. A.* **16**, 4135) to the relative positions of neighboring mols., and by Hewlett (*C. A.* **17**, 680) to a cryst. structure in liquids, may be explained without such special assumptions in the same way as the mol. scattering of light in the preceding abstract. The liquid mols. serving as diffracting-centers are arbitrarily oriented and distributed uniformly in space, subject only to such variations as gave rise to fluctuations in d. in accordance with the Einstein-Smoluchowski formula: $\Delta\rho^2 = (RT^3/V)\rho^2\beta$, where $\Delta\rho^2$ is the mean. sq. d. fluctuation, ρ is the mean d., β the compressibility, and V the elementary vol. The wave lengths of X-rays are smaller than the av. mol. distance; hence the structure gives rise to diffraction rings more or less well defined according as the fluctuations in d. are small or large.

G. L. CLARK

Quanta of the ideal monatomic gas. K. SHAPOSHNIKOV. *Bull. Inst. Polyt. Ivanovo-Voznesensk.* **6**, 105-24(1922).—A mathematical paper, in which the quantum theory is applied to gases at high and at low temp.

J. C. S.

Negative valency and coordination number. E. A. SHILOV. *Bull. Inst. Polyt. Ivanovo-Voznesensk.* **6**, 281-90(1922).—The most pronounced negative affinity is accompanied by non-metallic properties, so that, if it is assumed that negative affinity is the result of a tendency of the rings of valency electrons to attain satn., it becomes necessary to make the supplementary assumption that only non-metallic rings of a

special type exhibit such tendency. It is suggested that the origin of complex compds. may be represented on an analogous principle, coordinative affinity arising as a result of the tendency towards satn. of non-dissociating, non-metallic at. skeletons. J. C. S.

The low-temperature-research station at Cambridge, England. L. F. NEWMAN. *Commonwealth Eng.* 10, 170-3(1922). W. H. BOYNTON

Notes on the furnishing and equipment of chemical laboratories. CHARLES A. KRANE, JAMES C. PHILIP AND ALEXANDER SCOTT. *Chem. Eng. Mining Rev.* 15, 121-3 (1922).—A general description of approved equipment in different countries. C. C. D.

Filtrations without paper and funnel. CARL SCHIERHOLZ. *Pharm. Monatshefte* 4, 2-4; *Oesterr. Chem.-Ztg.* 26, 9-10(1923).—A discussion of the adaptation of certain large-scale technical operations to lab. conditions, involving sand, pledgets of plant, animal or mineral wool, and bacteria filters. W. O. E.

Several methods of preparing ultra-visible protein sols and their significance for colloidal chemistry and biology (FODER) 11A. The hydrogen electrode in alkaline solutions (ATEN) 4. X-ray examination of the inner structure of strained metals (ONO) 9. New aids for Röntgen spectroscopy (SYNTZING) 1.

ALAMELLE, E. and FLAMAND, F. *Cours de physique et de chimie*. Paris: Felix Alcan. Fr. 7.50.

Annual Reports on the Progress of Chemistry for 1921. Vol. XVIII. Issued by the Chemical Society. London: Gurney and Jackson. Reviewed in *Physiol. Abstracts* 7, 153(1922).

Annual Tables of Constants and Numerical data: Chemical, Physical and Technological. Vol. IV, Parts I and II combined. London: E. C. 4. Cambridge University Press, Fetter Lane. £7. Reviewed in *Analyst* 48, 46(1923); cf. *C. A.* 16, 1903.

ATACK, F. W. *Chemists' Year Book*, 1923. 8th ed. 2 Vols. New York: Chemical Catalog Co., Inc. \$6.00.

BULL, P. G.: *Chemistry of To-day. The Mysteries of Chemistry Lucidly Explained in a Popular and Interesting Manner. Free from all Technicalities and Formulae*. Philadelphia: J. B. Lippincott & Co. 311 pp. \$2.75. Reviewed in *Ind. Eng. Chem.* 15, 322(1923).

DEI TORRE, G.: *Trattato di chimica generale*. 6th Ed. Milan: Società editrice Dante Alighieri. 812 pp. £ 12.

EUCKEN, ARNOLD.: *Grundriss der physikalischen Chemie für Studierende der Chemie und verwandter Fächer*. Leipzig: Akudem. Verlagsgesellschaft. 492 pp. M 220, bound M 270.

GAUTHIER-ÉCHARD, MME. B.: *Manuel de chimie*. 12 Ed. Revised. Paris: Fern. Nathan. 373 pp.

GRANDMONTAGUE, H., GRANDMONTAGUE, MME. and ROUDIL, A.: *Cours expérimental de chimie à l'usage des écoles primaires supérieur et des cours complémentaires (garçons et filles)*. Paris: Larousse.

LESPIEAU, R. and COLIN, CH.: *Cours abrégé de chimie*. Paris: Hachette. Fr. 6.

LESPIEAU, R. and COLIN, CH. *Cours et expériences de chimie*. Revised Ed. Paris: Hachette.

LIHSENGANG, RAPHAEL, ED.: *Kolloidchemie 1914-22*. Dresden and Leipzig: Th. Steinkopff. 1914-22. Dresden and Leipzig: Th. Steinkopff. 100 pp. M 60.

MÉYRAL, P.: *Cours de chimie*. Paris: Masson & Cie. Fr. 9.

MÉYRAL, P.: *Cours de physique et de chimie*. 5th Ed. Revised. Paris: Masson et Cie. Fr. 8.

OSTWALD, WOLFGANG, WOLSKI, P. and KUHN, A.: *Kleines Praktikum der Kolloid Chemie*. 4th Ed. Revised. Dresden and Leipzig: Th. Steinkopff. 172 pp. 3s 4d.

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

Some interesting tracks of alpha particles in gases. R. W. RYAN AND W. D. HARKINS. *Nature* 111, 114(1923).—Three photographs (to be discussed later) are given. E. J. C.

The production of radioactive substances. C. ULRICH. *Z. angew. Chem.* 36, 41-2, 49-52, 54-5(1923).—The methods are given for sepg. the U, Ra, Act and Io from their minerals. M. FARNSWORTH

A study of some radiations of neon in view of their applications to meteorology. ALBERT PÉREARD. *Compt. rend.* 176, 375-7(1923).—Using the Michelson interferometer, P. detd. the mean wave lengths of six of the luminous radiations of Ne. M. F.

Theory of the thermionic currents. R. GANS. *Ann. Physik* 69, 385-408(1922).—A theoretical mathematical consideration of vacuum tube characteristics. G. L. C.

Luminescence centers and variations in gas pressure caused by electric discharges in spectrum tubes. I. I. L. HAMBURGER. *Z. Elektrochem.* 28, 545-53(1922); cf. *C. A.* 15, 1459. H. JERMAIN CREIGHTON

Quantum theory of line spectra. N. BOHR. *Kgl. Danske Videnskab. Selskab. Skrifter, naturvidenskab. math. Afdel.* [8] 4, 1-100(1918).—Theoretical. The quantum theory of line spectra is developed with special reference to the H spectrum, and to the Stark and Zeeman effects. J. C. S.



Absorption of light by chlorine. H. V. HALBAN. *Z. Elektrochem.* 28, 496-9(1922); cf. *C. A.* 17, 923. H. JERMAIN CREIGHTON

Stability of atom nuclei, the separation of isotopes, and the whole number rule. W. D. HARKINS. *J. Franklin Inst.* 194, 645-81, 783-814(1922); 195, 67-106(1923).—A review. Cf. *C. A.* 16, 4125. JOSEPH S. HEFBURN

The dimensions of the atomic nuclei and their relation to α , H^+ , β and γ radiation. M. C. NEUBURGER. *Ann. Physik* 70, 189-52(1923).—N. presents calcs. of the radii of the nuclei of all of the elements based on the ranges of α , H^+ and β rays. W. ALBERT NOYES, JR.

Quantum theory of the hydrogen molecule-ion. K. F. NIESSEN. *Ann. Physik.* 70, 129-34(1923); cf. *C. A.* 17, 359.—The work of N. amplifies that of Pauli, but their results are slightly at variance. N. calcs. for the model of the H mol. ($n_1 = 0$, $n_2 = 1$, $n_3 = 1$) energy = $-0.516 Rh$ (R = Rydberg const.), distance between nuclei = $5.53 a_1$ (a_1 = wave length of the shortest radiation of the H atom), eccentricity of the ellipsoid = 0.780, the greatest error being in the last decimal place in each case. N. has in addn. made similar calcs. for all cases in which $n_1 + n_2 + n_3 \leq 6$, and has calcd. the ionization potential of the H_2 mols. for all of these cases. N. also points out that Franck probably was premature in forsaking his original standpoint that a potential of 30.5 v. the H mol. is completely dissociated into its constituent parts. W. ALBERT NOYES, JR.

Structure of the sulfur dioxide molecule. A. O. RANKINE AND C. J. SMITH. *Proc. Phys. Soc. London* 35, Pt. I, 33-8(1923).—Dimensionally it may be assumed that the SO_2 mol. would have the properties of a particular arrangement of two Ne atoms and one A atom. R. and S. have calcd. the mean area which such a model so constituted would present in collision for all orientations and compared the result with the mean collision area deduced from detns. of the viscosity of the gas. The computed mean

collision area for the model  is 0.99×10^{-16} cm.², while the actual mean collision area of SO₃ as derived from viscosity measurements is 0.94×10^{-16} cm.². The authors suggest that the most probable arrangement is that in which chem. bonds exist between each of the 3 atoms corresponding to the formula .

L. T. FAIRHALL

Experiments on separating elements and isotopes by diffusion. ERNST MURMANN. *Oesterr. Chem.-Ztg.* 26, 14-5(1923).—Expts. showed that salts of Ni and Co could be partially sepd. by diffusion, so this method serves to identify elements in the ordinary sense of the term. But even tedious and laborious attempts to sep. U, Cl and Li salts into isotopes by the same method were unsuccessful. This is probably due to the fact that the at. vols. of elements are different, but those of isotopes of a given element are the same, and the mobility of the ion is dependent upon the at. vol., rather than upon the at. wt.

W. C. EBAUGH

Variation of "emanating-power" with temperature. A new secondary radium-emanation standard. J. H. L. JOHNSTONE. *Trans. Roy. Soc. Canada* 15, Sect. 3, 101¹-9(1921); *Science Abstracts* 25A, 478.—The variation of emanating power with temp. has been detd. for certain specimens of carnotite and uraninite. By heating the minerals to a high temp., the temp. coeff. of the emanating power is greatly decreased so that for ordinary ranges of lab. temp. it may be assumed to be negligible. A secondary emanation standard has been suggested which can be easily and simply prepd., which is not subject to appreciable variations under ordinary conditions and which is more convenient to use, particularly in the field, than either the customary standard Ra soln. or a U mineral of known compn.

H. G.

Changes in the charge of an α -particle passing through matter. G. H. HENDERSON. *Proc. Roy. Soc. (London)* 102A, 496-506(1922); cf. *C. A.* 17, 21.—Beams of α -rays, reduced in velocity by passing through absorbing material, were deflected by a magnetic field and studied photographically. A new band was obtained half way between the undeflected and the normal deflected beam. This is ascribed to α -particles which have picked up one electron when the velocity has fallen to 800,000 v. Another band due to neutral α -particles was obtained. The hypothesis is advanced that an α -particle may pick up and lose electrons several times on its path.

W. ALBERT NOYES, JR.

A preliminary investigation of the intensity distribution in the β -ray spectra of radium B and C. J. CHADWICK AND C. D. ELLIS. *Proc. Cambridge Phil. Soc.* 21, 274-80(1922).—A further contribution to the Ellis (cf. *C. A.* 16, 2071, 3434, 3805)—Meitner (cf. *C. A.* 16, 3030) controversy in regard to the origin of β -ray spectra. Using the ionization method, the authors measure the intensity distribution in the β -ray emission of Ra B and C. Only about 20% of the continuous spectrum can be accounted for by scattering. The magnitude is roughly what would be expected if each disintegrating atom contributed one electron to the continuous spectrum. More accurate expts. are in progress.

MARIE FARNSWORTH

Note on the curved tracks of β -particles. P. L. KAPITZA. *Proc. Cambridge Phil. Soc.* 21, 129-35(1922).—To explain the curvature in the paths of β -particles in the photographs taken by the Wilson expansion app., K. calcd. the magnetic moment which a particle must possess in order to produce an appreciable curvature in its path. The magnetic moment is very large so that the curvature cannot be explained quant. by means of magnetic moments in the particles.

M. FARNSWORTH

Photoelectric effect of ultramicroscope particles. R. BÄR AND Y. C. YANG. *Arch. sci. phys. nat.* 4, 249-52(1922); *Science Abstracts* 25A, 724.—Particles of radius (2 to 14) $\times 10^{-1}$ cm. obtained by evap. Se in dry air were maintained in suspension in a Millikan

condenser and subjected to the ultra-violet rays from a Hg arc. By using Einstein's equation, $h(\nu - \nu_0) = \frac{1}{2}mv^2$, as applied to the expts., it was found that they gave a new proof of the non-existence of subelectrons. H. G.

What is the cause of the apparent existence of subelectrons on ultramicroscopic particles? E. REGENER. *Naturwissenschaften* 11, 17-21(1923).—A discussion with numerous references. It is considered that the idea of subelectrons is disproved (cf. C. A. 14, 3579) and that the apparent existence of subelectrons can be explained by errors in measuring the thickness of adsorbed gas films (cf. C. A. 14, 3015); König, C. A. 17, 661. C. C. DAVIS

A method for the determination of the nature of ions formed by the collision of slow electrons. H. KALLMAN AND P. KNIPPING. *Naturwissenschaften* 10, 1014 (1922).—It has been proved by various investigators that to ionize a mol., a sp. amt. of energy in the electron, varying for each mol., is necessary, but the nature of the ions has not been detd. A small slit in the app. where collision of the electrons and mols. occurred allowed the passage into a 2nd evacuated chamber of ions of low velocity. The ions were then accelerated to a definite velocity and rendered parallel by an elec. field. This ionic beam was passed through a diaphragm into a space where it was deflected by a transverse magnetic field. From the deflection and the strength of the elec. and magnetic fields, the ratio e/m was detd. From the magnetic field, the ions were caught on a Pt wire and identified electrometrically. C. C. DAVIS

A study of the luminous discharge in iodine. A determination of the ionization potential of iodine. W. A. NOYES, JR. *J. Am. Chem. Soc.* 45, 337-42(1923); cf. C. A. 16, 3809.—By using the method described previously the ionization potential of I is found to be 10.0 ± 0.2 v. This probably corresponds to the equation $I_2 = I + I^+ + \oplus$. A higher multiple of the ionization potential for a tube of given length is found than in the case of H and Hg, owing to the electron affinity of the gas. W. A. NOYES, JR.

The theory of ionization by swiftly moving electrified particles and the production of characteristic X-rays. SVEIN ROSSELAND. *Phil. Mag.* 45, 65-83(1923).—The theory of ionization by swiftly moving elec. particles is discussed in its relation to (1) the expts. of Millikan (C. A. 16, 1041) and of Wilkins (C. A. 16, 1905) on the production of bivalent ions in He by α -rays, (2) the increase of intensity of characteristic X-rays with increasing voltage, and (3) the occurrence of certain lines in the X-ray series which are due to multiple ionization of the inner electronic groups (enhanced lines). The phenomenon of multiple ionization of an atom produced by the action of a single particle is directly connected with the dimensions of the different electronic groups. In this manner the dimensions of the electronic orbits in He are calcd. from Millikan's expt. and found to be of the order predicted by Bohr's theory. The expts. on the dependency of intensity of characteristic X-rays on voltage afford a direct means of investigating the no. of electrons in the inner groups of the heavier atoms and the dimensions of these groups. The appearance of X-ray lines originating from doubly ionized atoms is discussed and it is concluded that these lines are excited by a single impact of an electron on the atom and not by successive impacts. S. C. LUND

Comparison of the thermionic and photoelectric work function for platinum. O. KOPPIUS. *Phys. Rev.* 18, 443-55(1921); *Science Abstracts* 25A, 493.—The work function, or work necessary to detach an electron photoelectrically from Pt, was found to be 4.80 v., which is close to the values found for the corresponding thermionic work function. The relative energy of spectrum lines of Hg, 2301 to 2804 Å. from an arc in quartz, after dispersion by a quartz spectrograph, was detd. with a Coblentz thermopile. H. G.

The Thomson effect. O. M. CORBINO. *Atti. accad. lincei* 30, II, 33-7(1921); *Science Abstracts* 25A, 727.—The ordinary method of computing the Thomson effect

on the electronic theory of metals is compared with Lorentz's; it is shown that Lorentz uses underlying assumptions which assimilate his conception of electrons in a metal to that of a gas in a porous body.

H. G.

Theory of Röntgen spectra. II. ADOLF SIEGAL. *Sitzb. Akad. Wiss. Wien* 129, 635-60(1920); cf. *C. A.* 14, 2581; 15, 337.—The error introduced by the use of the Loschmidt no. in the standard value for the lattice const. of NaCl is considered. Attention is also directed to a theoretical $L\alpha$ arrangement which takes account of the relativity correction. The hypothesis used in the proof of the electron ring theory may be reduced to Bohr's frequency hypothesis. The presence of 3 electrons in the K ring follows qualitatively from the assumption of a spacial arrangement of electrons in the sheath. The detn. of the quantum conditions of the L and M electrons permits the no. of L and M absorption edges to be obtained.

J. C. S.

X-ray crystallography, X-ray wave lengths, space lattice dimensions and atomic masses. L. W. MCKEEHAN. *Science* 56, 757-9(1922).—The following numerical values are recommended as most probable: calcite grating space, 3.028×10^{-8} cm. rock salt grating space, 2.81355×10^{-8} cm.; no. of mols. per mole 6.0594×10^{23} ; Mo $K_{\alpha 1}\lambda = 0.70783$ and $K_{\alpha 2}\lambda = .71212$ Å.

G. L. CLARK

The excitation of characteristic X-rays from light elements. J. C. McLENNAN AND (MISS) M. L. CLARK. *Proc. Roy. Soc. (London)* 102A, 389-410(1923).—Using the method adopted by Hughes (*C. A.* 16, 1044, 1358, 1704), the crit. absorption wave lengths of the K and L series were detd. for B, Be and Li and of the L series for C, with the following results: C, L series, $\lambda = 166.7$ Å. (74.0 v.); B, K series, $\lambda = 83.6$ Å. (147.5 v.); B, L series, $\lambda = 292.2$ Å. (42.2 v.); Be, K series, $\lambda = 118.2$ Å. (104.3 v.); Be, L series, $\lambda = 428.1$ Å. (28.8 v.); Li, K series, $\lambda = 290.8$ Å. (42.4 v.); Li, L series $\lambda = 1019.0$ Å. (12.1 v.). The Moseley linear law connecting the square roots of the frequencies of the crit. absorption K series wave lengths with the at. nos. of the elements applies not only for the heavier elements but also for the lighter ones down to Li. The results fit in with the view that the Lyman ultra-violet series for H is the K X-ray series of this element, and that the convergence wave length of the K series of He is approx. $\lambda = 485.5$ Å. The square roots of the crit. potentials representing the convergence wave lengths of the L series and the first members of the L series are in both cases proportional to the at. nos. Apparently the Moseley law, which is known to apply for the L series of the heavier elements, ceases to apply for elements lighter than Å.

G. L. CLARK

The Röntgen rays of the cathode from the auto-electronic charge. J. F. LILJENFELD. *Physik. Z.* 23, 506-11(1922).—It is found that under certain conditions X-rays are emitted from the cold cathode of a suitable tube. These are of sufficiently high frequency to pass through the glass walls of the tube and through Al. Numerous possible explanations are presented; e. g., the atoms in the tip of the cathode are in so powerful a field as compared with those lying below that electrons may change orbits. No light or heat apparently is produced; hence the effect would necessarily be confined to innermost orbits. Or again under certain conditions of the ionization of residual gas electrons may impinge on the cathode and produce rays by the usual anticathode process. Following the paper a lengthy discussion by Wien and Schottky throws considerable doubt not only upon the various mechanisms but upon the actual nature of the phenomenon.

G. L. CLARK

The action of radiations. II. FR. DESSAUER. *Z. Physik* 12, 38-47(1923).—There is put forth a working hypothesis concerning the absorption of X-rays in biological tissues, photographic plates, colloids and other substances. According to this hypothesis the energy is stored in the centers of absorption according to the law of probability. This energy is equal to the energy which the excited mol. or atom gives up when it

returns to its normal state after the radiations are withdrawn. The number of particles affected at least once by the radiations is an exponential function of the time of exposure. From this it is evident that the substance must be exposed for an infinitely long time in order that all the particles be acted on at least once by the radiations. The theory seems to be in agreement with the observations of Dr. Wood on the effect of long exposures of X-rays on tumors.

A. W. SMITH

The action of radiations. MARIETTA BLAU AND KAMILLO ALYENBURGER. *Z. Physik* 12, 315-29(1923).—The authors develop mathematically the theory suggested by Dessaur (preceding abstr.) to account for the effect of Röntgen rays on biol. tissues, etc. An application of the theory is made to Röntgen-ray therapy, to the action of Röntgen rays on photographic plates and to the action of visible light on photographic plates. Agreement between the theory and the observations are found in these cases.

A. W. SMITH

A contribution to the acceptance of international normals of wave length. FRIEDRICH MÖLLER. *Z. wiss. Phot.* 22, 1-20(1922).—The wave lengths of lines in the Fe spectrum have been measured afresh with all possible precautions to the third decimal place. The results are given in tables and a crit. comparison is made with previous detns.

G. R. FONDA

Remarks on group spectra. E. GEHRCKE. *Physik. Z.* 23, 432-3(1922).—Attention is called to further regularities in the Fe spectrum similar to those reported in *C. A.* 16, 202, and it is further noted that similar groups of lines are to be found in the spectra of H and other elements whose spectra are rich in lines.

K. BURNS

Spectrum of hydrogen. S. BARRATT. *Science Progress* 17, 242-51(1922).—The major portion of this review of recent work is devoted to the secondary spectrum, though some attention is also paid to the series spectrum.

JOSEPH S. HEPBURN

The influence of the Doppler effect on spectroscopic fine structure and its elimination. NIKHILRANJAN SEN. *Physik. Z.* 23, 397-9(1922).—The positions of the lines of a very close group are dependent upon the temp. at which the spectrum is excited. Formulas are given which show the positions of these lines at any other temp. The procedure is applied to the $H\alpha$ line.

K. BURNS

The spectra of argon, iodine and nitrogen in the electric field. W. STREUBING. *Physik. Z.* 23, 427-32(1922).—In all cases the field weakens the continuous and band spectra. In the case of N only the heads of the bands could be well observed in strong fields. S. concludes that the decrease of intensity is not due to a change in the no. or velocity of the canal rays, or other secondary effect of the field. In case of I the continuous and band spectra could not be photographed. Several of the lines, present in the canal rays or the spark spectrum, were observed in the field. Six lines between 4548 and 4600 Å. showed two components, one perpendicular and the other parallel to the field. The remaining lines showed only the parallel component. A new line of great intensity was brought out by the field at 4280 Å. Several I lines were displaced either toward shorter or longer wave lengths. A was unaffected by the field.

K. BURNS

A theory of dispersion in a system of asymmetric dipoles. WALTER GORDON AND HARMUT KALLMANN. *Ann. Physik* 70, 121-8(1923).—A mathematical paper in which the dispersion and the n in a system of dipoles are calcd. G. and K. have their calcs. on a system of dipoles capable of linear oscillation, assuming that only one charge is capable of movement along the axis of the dipole.

W. ALBERT NOYES, JR.

Studies on the low-voltage arc in mercury vapor and its relation to fluorescence. Y. T. YAO. *Phys. Rev.* 21, 1-21(1923).—A discussion is given of the effect of velocity of thermal emission of electrons from a heated filament on the potential necessary to maintain a low-voltage arc. Comparison of the results of Y. with those of others shows

that this correction is from 2 to 3 v. A table is given from which the proportion of electrons having energies above any value for any filament current can be computed. Measurements of the min. arc voltage were made as follows: (a) with an anode of liquid Hg; (b) with a Ni anode and liquid Hg at distances of 7 and 180 cm.; (c) with a Ni anode and Hg in a sep. reservoir connected to the discharge tube by tubes of varying length; (d) with the discharge tube so arranged that the arc could be observed either in a stream of Hg vapor or with stationary vapor. The voltage necessary to maintain the arc decreased with increasing filament current, becoming const. For case (a) with high filament currents the arc struck at 5.5 v., the difference between the ionization potential (10.4 v.) and the resonance potential (4.9 v.). The atoms were therefore ionized by two successive impacts. In case (b) the arc voltage was 1.21 v. higher with liquid Hg at a distance of 180 cm. than at a distance of 7 cm. Results were analogous in case (c), and in case (d). This indicates that at some distance from the Hg surface the radiation λ 1849 det. the arc voltage rather than λ 2536. Conclusion: Some influence increases the probability of ionization along the $1S - m\bar{p}_1$ path as compared with the $1S - m\bar{p}$ path in freshly distd. vapor.

W. ALBERT NOYES, JR.

• Practical method of reading photographs taken with the Féry spectrograph. H. PERPÉROT. *Recherches et inventions* 4, 75-8(1923).—The spectrograph is so constructed that the field is divided into 5 horizontal superposed portions. A photograph is taken of the C arc spectrum, so that it will come in position 3; while in position 2 is placed a 20-cm. scale accurately divided into 1,000 divisions. Another plate is then taken with arc spectrum in position 1 and the spectrum of one or more pure metals (Al, Ag, Zn, Fe, etc.) in position 3. After developing, fixing, and drying, the two negatives are suitably fixed together, gelatin sides touching, so that the C-arc lines of the two will exactly coincide, and are examd. with a magnifying glass so as to standardize the scale in terms of wave lengths. Finally, a photograph is taken of the C arc (in position 1) and of the sample to be examd. (in position 3); and the plate is then examd. by fixing to the scale as before. Glass plates must be used, as the dimensions of films change with temp. and hygrometric conditions. The accuracy is about 2 Å. in the red and 0.2 at the ultra-violet end of the spectrum.

A. P.-C.

Absorption spectra of triphenylmethane coloring matters. EMILIO ADINOLFI. *Atti accad. Lincei* [v] 31, i, 461-4(1923); cf. *C. A.* 16, 2265.—Solns. of 19 of these coloring matters in water and in Me, Et, isobutyl, and Am alcs. have now been examd. spectroscopically by the diffusion method (*C. A.* 15, 2034), the positions of the mid-points of the two absorption bands being tabulated. With the alc. solns. the velocity of diffusion is greater than with those in other solvents, this velocity diminishing as the mol. wt. of the alc. increases. The diffusion of some of the compds. examd. is characterized by two distinct phases: the first consists in a rapid propagation of the coloration with a very low gradient of the concn., the spectrum showing only one of the characteristic bands which assumes const. breadth; the original surface of sepn. remains and gives rise to a second, slower diffusion, as a result of which the absorption curve characteristic of this group of compds. becomes complete. That this phenomenon of double diffusion appears to be due to two different at. groupings is supported by other evidence to be published later. The gradual displacement of the maxima of the absorption curves as the mol. mass of the alc. solvent increases is observed with all the compds. examd. with the exception of uranine and rhodamine-B.

J. C. S.

Arc between carbon and mercury electrodes. A. SELLERIO. *Nuovo cimento* 23, 31-57(1922); *Science Abstracts* 25A, 366-7.—The arc stream between Hg (+) and C (—) in air at small currents is a tranquil jet of green vapor without surrounding flame. Expts. were carried out with the object of detg. the velocity of the arc stream.

The jet is always normal to the crater which is a circular depression (3 to 5 mm.) surrounded by a ring of Hg oxide. Figures are given to illustrate the growth of current and voltage to a stable condition of the arc. Measurements were made of the rate of Hg consumption in a given time, with a known current and crater diam. The ionization coeff. (proportion of atoms leaving the electrode which take part in the transference of electricity) was of the order of $\frac{1}{5}$ and the velocity of the stream was between 10 and 30 m. per sec. This is in agreement with similar measurements which have been made by other means. The current d. is high, being of the order of 300 to 1000 amp. per sq. cm. The crater area varies directly as the current. Curves are given to exhibit the variation of voltage with arc length at const. current. The relation is approx. linear. The cyanogen spectral lines are absent in this arc. H. G.

Interference phenomena in non-homogeneous light. N. K. SETHI. *Proc. Indian Cultivation Science* 7, Pts. 1 and 2, 37-46(1921); *Science Abstracts* 25A, 463; cf. *C. A.* 16, 2281.—In Lloyd's expt. if a retarding plate of glass immersed in a liquid of nearly equal n is introduced in the path of one of the interfering beams, a very large no. of fringes are obtained. The interposition of colored screens reduces the no. of fringes. No band may be described as central, and the width of the fringes, too, is not const., but varies continually from one end of the field to the other. This is shown to be due to what may be called the dispersion of the achromatic band, which causes different groups of waves in the spectrum to produce max. visibility of the fringes in different parts of the field. Newton had observed that the no. of white-light fringes seen in a thin plate is increased considerably by viewing them through a prism. Rayleigh explained this as being due to the formation of an achromatic system of fringes, the necessary condition for which is that the thin plate should be bounded by curved surfaces; and according to him this phenomenon could not be expected in a truly wedge-shaped plate. S. has, however, observed it even in the case of an air film between two interferometer plates, and has shown that an achromatic system of fringes is not needed to explain Newton's observations. The dispersion of white-light fringes referred to above is sufficient to explain not only the increased no. of fringes, but also to give a color distribution corresponding almost exactly with Newton's observations. H. G.

Dispersion of light in fluorescent solutions. A. CARRELLI. *Atti accad. Lincei* 31, i, 157-60(1922); *Science Abstracts* 25A, 717-8.—With fluorescent substances exhibiting pronounced absorption and intense fluorescence, it appears possible that there exist two distinct types of vibrators, and hence two corresponding anomalies in n , one referring to the zone of emission and the other to that of absorption. By means of the Jamin refractometer aq. solus. of various substances of the triphenylmethane group have been investigated, the iridescent fringes obtained with a powerful source of light being analyzed spectroscopically. The results indicate that, in fluorescent substances, the presence of emitting vibrators modifies the dispersion curve in a manner similar to that observed with absorbent vibrators. The various substances examined differ as regards the magnitude and distribution of this effect. H. G.

The problem of the fine structure of the Balmer lines. W. BORNE. *Naturwissenschaften* 11, 45-6(1923).—The data reported by Gehrecke and Lau (cf. *C. A.* 16, 3261) for the components of the Balmer lines are maintained not to refute the special theory of relativity, but only to show that the conditions for applying the special theory are not present. The movement of the electrons cannot be regarded as quasi-stationary, and their form does not correspond to the Lorentz contraction. The true form is detd. by internal forces which are still unknown, but it is intelligible if the Lorentz contraction is assumed not to manifest itself because of rapid periodic change of direction.

C. C. DAVIS

Chemoluminescence. I. A. A. GRINBERG. *J. Russ. Phys. Chem. Soc.* 52,

151-85(1920).—A summary is given of previous work on this subject, particularly on bioluminescence (cf. Radziszewski, *Ber.* 60, 321(1877); Lenard and Wolf, *Ann. Phys. Chem.* [2] 34, 918-25; Trautz, *Z. physikal. Chem.* 53, 1-111(1905); Trautz and Schorigin, *Z. Elektrochem.* 11, 306-7(1905); Dubois, *C. A.* 6, 3098; Harvey, *C. A.* 10, 3077; 11, 2906; Goss, *C. A.* 11, 2906). The light effect obtained with the system, pyrogallol- H_2O_2 - KMnO_4 under various conditions has been investigated, the intensity of the light being measured photographically. At 16-17° the greatest intensity was obtained with a mixt. of 4 cc. of 0.005 *M* KMnO_4 , 2 cc. of 0.01 *M* pyrogallol, and 2 cc. of 3-12% H_2O_2 solns. H_2SO_4 in the concn. 0.018-0.04% weakens the effect considerably, while 0.0046-0.026% of KOH enhances it to a slight extent.

J. C. S.

A method of separating the arc and spark lines of emission spectra. W. WIEN, *Ann. Physik* 69, 325-34(1922).—Using the method previously developed for making canal rays visible, W. investigates the emission of light by charged and uncharged atoms. Canal rays which come from a narrow slit are allowed to pass through a short plate condenser which is maintained at suitable voltages by means of two small d. c. dynamos. The light-giving atoms are deflected against the plate of the condenser and they no longer emit light as moving atoms. The light emitted by these atoms is examd. by means of a prism spectrograph of hard flint glass or of quartz. In H there is no difference between the appearance of the spectrum when there is no voltage on the condenser and when 2000 v. are applied. It follows that the Balmer series is emitted by uncharged atoms. In O many of the lines are decidedly deflected by the action of the elec. field on the condenser. Two of these lines are, however, uninfluenced. The deflected lines belong to the spark spectra and the undeflected lines to the series spectrum. The first are sent out by charged atoms; the latter, by uncharged atoms. The behavior of N is complicated. It is not possible in this case to make a sepn. into series and spark lines. Strong positive and negative bands are also present. Eight lines are found to be deflected. Of these, 4 according to Stark and Künzer, belong to sharp spark lines and 4 to diffuse spark line. Three lines are not acted on by the elec. field. Two of these belong to the arc spectrum. Observations on the deflections in the band spectra seem to show that the negative bands are produced by charged atoms and the positive bands by uncharged atoms. The Hg lines as a whole do not show any deflection. They are therefore due to uncharged atoms.

A. W. SMITH

Harmonics in ultra-red absorption spectra. CLEMENS SCHAEFER and MAX THOMAS, *Z. Physik* 12, 330-41(1923).—A study is made of the higher harmonics of the absorption bands in the infra-red region in gases and solids. The usual spectrometer method of observation is used with a radiometer as a detecting device. The second harmonic is found for CO at a wave length of 1.573 μ . The fundamental at 4.67 μ and the first harmonic at 2.35 μ were already known. The frequencies of these vibrations are not exactly as 1 : 2 : 3. The more exact theory of Sommerfeld gives the relation of the frequency of the fundamental to the frequency of the harmonics as: $\nu(1-x)$; $2\nu(1-2x)$; $3\nu(1-3x)$. The wave length of the second harmonic calcd. from this relation is 1.577 μ —a value in good agreement with the observed value 1.573 μ . In HCl the fundamental is at 3.46 μ , and the first harmonic at 1.76 μ . The second harmonic is found at 1.190 μ . This value agrees well with the value 1.192 μ , calcd. from Sommerfeld's equation. The first harmonic for HF was found at 1.27 μ . The fundamental is known to be at 2.52 μ but the second harmonic which should lie at 0.84 μ could not be investigated. The second harmonic for HBr should lie at 1.34 μ but this is too near the absorption band for water vapor to be investigated with certainty. Similar observations were made on some solids. The first harmonic for SrSO_4 is at 4.5 μ ; the second harmonic at 3.0 μ ; and the third harmonic at 2.35 μ . The frequencies of these vibrations are not in the exact ratios 1 : 2 : 3 : 4. In a SiC the fundamental is at 12 μ . The octave of

this band occurs at 6.24μ . The higher harmonics were not investigated. In calcite the absorption is too complex for such an analysis. A. W. SMITH

Influence of adsorbed ions on the photochemical sensitiveness of silver bromide. K. FAJANS AND W. FRANKENBURGER. *Z. Elektrochem.* 28, 499-505(1922).—A lecture based on expts. by Frankenburg, the details of which are to be published shortly. Various phenomena which take place in the interior of analogous crystals under the influence of light, support the idea that the "inner photo-elec. effect" with Ag halides is not associated with the metallic component, as usually supposed, but with the anion. Spectral (optical) sensitization of AgBr by Ag or OH ions represents the simplest and clearest case of this kind. The excess adsorbed Ag ions act as electron acceptors which are more active than the normal Ag ions of the lattice surface, on account of the changed configuration of the electrostatic field. Sensitization by adsorbed OH ions (O ions) is a polar counterpart of the foregoing, and may be traced back to a primary decompn. of the adsorbed layer of Ag_2O (AgOH). The influence of moisture on the sensitiveness of AgBr is due to the fact (1) that H_2O vapor may function as a Br acceptor and (2) that it causes hydrolysis of the surface of the AgBr with the formation of the oxide, which has been detected in expts. carried out at higher temps. Sensitization by many other anions (e. g., the anions of certain dyes) is analogous to that by OH ions. The influence of adsorbed ions on the photochem. sensitiveness of AgBr is the result of a marked interference in the system that is subjected to the action of light. Accordingly, the spectral sensitization attained is very far reaching. However, in many instances of adsorption, the resulting change of the field of force may involve only a greater or smaller change in the energy consumed in the passage of electrons between normal ions of the surface of the Ag halide. H. J. C.

Increase and distribution of valence as a primary effect of light. R. KÖGEL. *Phot. Korr.* 59, 35-9(1922).—The primary action of light on chem. compds. is to increase the valence, resulting in a rearrangement of the valency bonds and an increase in the energy of the system. The valence increase leads to the formation of addn. compds. and the final product may show either an increase or decrease of energy. The cases of O, N, and C are discussed. Structural formulas are given. L. DGER

Photolysis of carbonic acid. EMIL BAUR AND A. REBMANN. *Helvetica Chim. Acta* 5, 828-32(1922); cf. Baly, *C. A.* 16, 3463.—Upon repeating the work of Moore and Webster (*C. A.* 8, 352), with colloidal Fe and U oxides, $FeCl_3$ or $Na_2O \cdot 3UO_3$ as catalysts, no trace of CO_2 photolysis could be discovered. C. J. WEST

Contributions to the understanding of chemical actinometers. A. BENRATH, E. HESS AND A. OBLADEN. *Z. wiss. Phot.* 22, 47-64(1922).—For investigation of variations in the photochem. activity of daylight, Eder's soln. can be used only within limits. Actinometers depending on the reduction of $FeCl_3$ or the oxidation of oxalic acid in the presence of a U salt are equally good, but the action in each is retarded by the presence of electrolytes. The explanation lies in their depression of the dissociation and signifies that both these photochem. reactions are produced by ions only. G. R. F.

The photochemical reduction of titanium salts. A. BENRATH AND A. OBLADEN. *Z. wiss. Phot.* 22, 65-72(1922).—The reduction of $TiCl_4$ by alc. (*C. A.* 9, 1723) is accompanied by autooxidation and formation of H_2O_2 . Reduction by mandelic or lactic acid is free from such complications, and under daylight or the Hg arc proceeds with a speed proportional to the concn. of the reducing medium and of the $TiCl_4$. The const. calcd. for a bimol. reaction however decreases somewhat with increasing concn. of the reagents, owing to the retarding effect of the HCl formed. Chlorides also retard the reduction, indicating an ionic reaction. The sulfate and oxalate are not reducible. G. R. FONDA

The scattering of X-rays in liquids (RAMAN) 2. The new element hafnium (COSTER, HUYBRY) 2. Sensitization of coagulation processes: Colloids as indicators of photo-electric effects (PESKOV) 2. New aids for Röntgen spectroscopy (STINTZING) 1.

ACHALME. Les théories de la structure atomique. Paris: Payot & Cie. 43 pp.

BOHR, NIELS.: Drei Aufsätze über Spektren und Atombau. Braunschweig: F. Vieweg & Son. 148 pp.

KOSSEL: Les forces de valence et les spectres de Röntgen. Paris: Albert Blanchard. 70 pp. Fr. 4.50.

LUCKINSH, M.: Ultra-violet Radiation. Its Properties, Production, Measurement and Applications. New York: D. Van Nostrand Co., 269 pp. \$3.50.

STARK, JOHANNES: Die elektrischen Quanten. Ind. Rev. ed. Leipzig: S. Hirzel. 95 pp. M 55, bound M 90.

UNGANIA, EMILIO: Elettroni e monomesoni. L'atomo, sua vera composizione e struttura; la nuova concezione dell' universo. Bologna; L. Cappelli. L 32.

Vanadium and radium from carnotite ores. W. F. BLEECKER. U. S. 1,445,660, Feb. 20. Finely divided carnotite ore residue is heated with HCl, CaF₂, Na silicate and NaNO₃ or other oxidizing agent in order to dissolve V and Ra compds.

4—ELECTROCHEMISTRY

COLIN G. FINK

The efficiency of a high-frequency induction furnace. G. RINAUD. *Recherches et inventions* 4, 26-33(1923).—In a previously described induction furnace (C. A. 16, 2081) other things being equal (capacity of the circuit, dimensions of the furnace and of the object) the amt. of heat absorbed by the object in the furnace depends on its elec. cond. For a given furnace and substance there is an optimum capacity which gives max. efficiency. The amt. of energy absorbed by the substance in the furnace is approx. proportional to its diam., not to its cross section. For a given height of the object, there is an optimum length of winding and an optimum number of turns per cm.

A. P.-C.

Present status of the electric furnace in refining iron and steel. J. A. MATTHEWS. *Chem. Met. Eng.* 27, 872-4(1922).

W. E. RUDER

Electric reduction furnace iron for a steel making base. R. C. GOSROW. *J. Elec. Western Ind.* 50, 16(1923).—This process finds economical application in the Pacific North West owing to natural resources and market conditions. Steel pig analysis is C 2-2 1/4%; Mn 0.5-1%; Si 0.4-0.8%; S and P under 0.05%. All elec. furnace irons need be graded on the basis of analysis only. The use of pig steel will stabilize the price of steel scrap and conserve the supply.

W. E. RUDER

Synthetic pig iron. MARCEL DIDIER. *La fonderie moderne* 15, no. 12, 2 1/2 pp. (1922); *Bull. Cleveland Techn. Inst.* 2, 825(1923).—D. reviews the advantages of the elec. furnace. A Heroult mixed type, using both arc and resistance heating, is employed for synthetic pig Fe. The furnace consists outwardly of a refractory brick lining braced at the 4 corners by angle-irons. The hearth is of graphite made of fragments of electrodes ground up and agglomerated hot with tar. There is a fan-shaped armature bedded in the hearth and connected to the transformer for the return current, also a graphite electrode dipping vertically into the furnace. Single-phase a. c. is generally used. A well made furnace should have a life of several yrs. The electrode is protected from oxidation by a sheet-Fe mantle or by a coating of paste composed of Na silicate and powdered asbestos. For a daily output of 16 tons, a furnace of 1,000 kw.

capacity is required, and the av. power-consumption is 950 kw. hrs. Electrode consumption, given efficient protection from oxidation, should not exceed about 8 kg. per ton metal. A description is given of the actual procedure of charging the furnace, and the following typical mixts. are cited: (1) for malleable: 500 kg. turnings, 30 charcoal, 15 limestone; (2) for foundry: 500 turnings, 25, 55% ore, 40 limestone, 50 coke. Burdens are calcd. approx., and then modified according to the resultant product, as it is difficult to make definite allowance in advance for volatilization losses. C. G. F.

Production of synthetic cast-iron. K. DORNHECKER. *Stahl u. Eisen* **41**, 1881-9(1921).—Scrap iron is mixed with an excess of coke and sufficient lime, and the mixt. is melted in an elec. furnace of the arc type in which the electrodes dip into the upper part of the charge so that heat is generated by resistance as well as by the arc. The resulting metal contains 3-4% C, and by suitable addns. 0.5-4.5% Si may be introduced. The S content is extremely low (max. 0.02%) owing to the desulfurizing action of the lime in the presence of the C. By suitable regulation of the P content of the material charged into the furnace, the amt. in the metal is kept below 0.1%. The installation for working this process at Aarau is described in detail, together with the thermochemistry and economics of the process. J. S. C. T.

Preparation of boron carbide from boric acid and carbon in the electric furnace. J. M. LOGAN. *Trans. Roy. Soc. Canada* **15**, Sect. 3, 58(1921); *Science Abstracts* **25A**, 643.—Boric acid was mixed in different proportions with graphite, charcoal, or electrode carbon, and heated to different temps. from 800° to 1800° in closed carbon tubes or plumbago crucibles by means of a granular carbon resistance furnace; some runs were made in the Moissan arc furnace. The best results were obtained by 2 hrs.' heating at over 1800° in crucibles turned from 4-in. carbon electrodes. Crystals of the same form were obtained whether C or boric acid was present to an excess of 25%. H. G.

Electric enameling furnace lowers rejections on stove parts. ANON. *Chem. Met. Eng.* **28**, 364(1923).—An elec. furnace for baking vitreous enamel on cast iron and sheet steel operates at 650-760°, and to a max. of 1093°, and has a connected load of 118 kw. at 230 v., 3-phase 60-cycle. Its capacity is 7 lbs. (3.18 kg.) of metal per kw.-hr. Ni-Cr heat units are mounted away from the sidewalls and are evenly distributed between the upper and lower compartments of the furnace. Running periods are economically arranged. Rejects average 4%. Economy in labor costs, time and space are advantages claimed.

W. H. BOYNTON

"Quarzillite." KUMMLER AND MATTER. *Bull. Schweiz. Elektrotech. Verein* **13**, 307-12(1922); *Science Abstracts* **25B**, 489.—This is a resistance material with negative temp.-coeff., manufd. by the firm of Kummeler and Matter at Aarau. It is made in the elec. furnace from a combination of quartz and C; it begins to oxidize at 1700°; the working temp. should not exceed 1200° to 1400°. The resistance curve shows a decrease of resistance up to 600°, followed by a slight increase up to 1200°, after which the resistance again decreases, till it is finally destroyed by oxidation. The material can be supplied in the form of rods, tubes, or plates, but the last form is not suitable for practical purposes. The cond. of the ends, to which the terminals are connected, is suitably increased so as to avoid damage to the conductors. Some practical applications are mentioned. H. G.

The total resistance of an electrolytic cell and the resistance of its electrolyte. RUDOLF PERCY. Univ. Basel, *Thesis* 1922, 88 pp.; 21 illus.—There are 4 methods available for detg. the true elec. resistance, r , of the soln. of a cell from the apparent elec. resistance, r' , of the soln.: (1) increasing the frequency; (2) increasing the electrode area; (3) increasing the electrode voltage; (4) increasing the resistance. In each case the limiting value of $r' = r$. P. used the Kohlrausch bridge, with a nickelin wire 0.1 mm. in diam. and 39.89 ohms d. c. resistance. The U-shaped and H-shaped cells were

of very small capacity and all detns. made at 18° . The range of frequencies was from 15 to 50,860 cycles. In place of the telephone a galvanometer and detector, in series, were employed. In the first expts. H_2SO_4 and Pt electrodes (smooth and platinized) were used; in the second, 30% ZnCl_2 soln. with Hg and Zn electrodes; in the third, concd. NaCl soln. with Pt and Hg electrodes; and in the last, max. cond. solns. of 14 different inorg. salts with Hg electrode. Numerous curves and tables are shown. In general the total resistance of a cell is composed of the resistance of the electrolyte plus that due to electrode effects; the latter differs within wide limits. With increasing frequency or voltage or electrode area or specific resistance of the electrolyte the resistance of the cell approaches a limiting value equal to that of the electrolyte. In most of the cell combinations tried, the resistance of the cell drops off rapidly at first as the potential is increased and then more gradually. However, in the Hg electrode and salts such as the alkali and alkaline earth halides, the resistance of the cell passes through a distinct max. at low frequencies; this max. gradually disappears as the frequency is increased. The max. is independent of the concn. of the electrolyte but different for different electrolytes. The reason for this max. in these exceptional cases is not given.

C. G. F.

Role of chromates in electrolysis for chlorate. A. V. PAMFILOV. *Bull. Inst. Polyt. Ivanovo-Voznesensk.* 4, 113-7(1921).—Chromate plays a triple part in the electrolytic production of chlorate in an acid soln. (1) It acts as a "buffer" salt, regulating automatically the kinetic acidity of the liquid. (2) It forms a film on the cathode and thus prevents reduction of the hypochlorite formed as an intermediate product. (3) This film protects the cathode from disintegration and hence allows the Pt electrodes to be replaced by those of metals more readily accessible, such as Cu. These effects of chromate are sp. and are not exhibited by any other compd. J. C. S.

Refining gold bullion with chlorine at the Ottawa Mint. A. H. W. CLAYVE AND P. W. BOND. *Eng. Mining J.-Press* 115, 236-7(1923); cf. *C. A.* 16, 724.—This process supplanted electrodeposition at the Ottawa Mint in 1913. Details are given. A. B.

Control of acidity in nickel deposition. W. BLUM AND M. R. THOMPSON. *Brass World* 19, 18-21(1923).—For a rough qual. test add 5-10 drops of a 0.04% alc. bromocresol purple to 50 cc. of filtered electrolyte. A greenish yellow shows "acid," a violet shows "alkaline," and a deep green shows "neutral" to the indicator (about $p_H = 6$). For quant. acidity tests the drop-ratio colorimetric test is given in detail with methyl red and bromocresol purple (cf. *C. A.* 16, 1912). When necessary to calc. the quantity of acid or alkali necessary to add to maintain the Ni soln. at a desirable p_H , the following titration is recommended. Add bromocresol purple indicator as given above. Titrate with 0.1 N NaOH, or 0.1 N H_2SO_4 to neutral green color. For each cc. of NaOH required add 0.080 g./l. to plating bath, and for each cc. H_2SO_4 required add 0.105 g./l. A $p_H = 5.7$ is recommended for best results. CHAS. H. ELDRIDGE

The hydrogen electrode in alkaline solutions. A. H. W. ATEN. *Trans. Am. Electrochem. Soc.* 43 (preprint) (1923); 7 illus.—When a H electrode, satd. with H, is in equil. with 0.1 N HCl, it is in the same state of equil. with N HCl, and vice versa. However, this is not the case when the solu. of an alkali is used in place of an acid. When the electrode in equil. with 0.1 N NaOH is put in N NaOH, or the reverse, a considerable time period is required to reach the new equil. The same phenomenon is observed in a more marked degree when the electrode is changed from 0.1 N NaOH to 0.1 N NaCl, or the reverse. The explanation is that the electrode in NaOH soln. becomes a H-Na solid soln. electrode, and that a change from alk. solns. of different concns., or from acid soln. to alk. solns., or the reverse, must require an appreciable period of time to allow the electrode to take on the proper concn. itself. A theoretical discussion is given of the electrode potentials under the varying conditions. CHAS. H. ELDRIDGE

Electrochemistry of non-aqueous solutions. I. Method of current density-potential measurement in the electrolysis of metallic salts in pyridine. ROBERT MÜLLER. *Monatsh.* 43, 67-74(1922).—A form of cell suitable for these measurements is described. The potential of the element $\text{Ag}|0.1\text{ }N\text{ AgNO}_3\text{ in C}_6\text{H}_5\text{N}$ has been measured and found to have the value, $e_h = +0.26\text{ v.}$ II. Decomposition potential and electrode potentials in the electrolysis of pyridine solutions of silver nitrate, and the potential of silver in these solutions. R. MÜLLER AND A. DUSCHEK. *Ibid.* 75-80.—Measurements have been made of the decompn. potentials of AgNO_3 solns. of different concns. The values decrease as the concn. of the electrolyte increases, from 2.15 v. for 0.1 $N\text{ AgNO}_3$ to 1.95 v. for a satd. soln. The potential of Ag against AgNO_3 solns. in $\text{C}_6\text{H}_5\text{N}$ increases slightly as the concn. of the soln. increases. The anodic potential difference for each concn. is a function of the current density. H. J. C.

Dezincification of brass. R. B. ABRAMS. *Trans. Am. Electrochem. Soc.* 42, 39-54(1922); *Metal Ind.* 20, 467-8(1922); 21, 66-7(1923).—Dezincification is defined as that change in brass (due to action of sea water over a period of years) which results in a porous mass of Cu replacing the original alloy. The product is weak and brittle; it has been shown to be redeposited Cu. Immersion of brass in $N\text{ HCl}$ will produce dezincification in a few weeks just as it occurs in nature after several years. Agitation of HCl soln. produces uniform corrosion only. The dezincification that takes place in still, dil. HCl is thought to be due to a membrane of insol. CuCl . With brass anodes (0.25 amp. per sq. ft.) dezincification again takes place in still 3% NaCl . If dil. NaCl electrolyte is agitated, or if strong electrolytes (such as concd. NaCl , concd. HCl , or sulfate solns.) are used which dissolve the CuCl membrane, the brass corrodes as a whole. The use of artificial membranes causes the dezincification of Cu in solns. which usually give complete corrosion. An adequate supply of dissolved Cu, maintained by using a Cu salt as electrolyte, will cause dezincification without any membrane whatever. CHAS. H. ELDRIDGE.

Reactions of the lead storage battery. M. KNOBL. *Trans. Am. Electrochem. Soc.* 43 (preprint) (1923).—Experimental runs were made on "Harvard" Type A pasted electrodes, one + and 2 — plates, 20 amp. hr. capacity, with from 0.10 to 10.0 amp. discharge rates. Careful record was kept of wt. and density of electrolyte, of Faradays, and calens. showed that almost exactly 2 mols. of H_2SO_4 were consumed per 2 Faradays. This supports the equation of Gladstone and Tribe that on discharge $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 = 2\text{PbSO}_4 + 2\text{H}_2\text{O}$, which indicates that the peroxide of Pb (and not a higher one as claimed by Féry) is formed on charge, and that 2 mols. H_2SO_4 are used per 2 Faradays on discharge. Expts. with Planté type positive show that the quantity of acid consumed decreases constantly as discharge continues. C. H. E.

Charging vehicle batteries. OTTO SARVAS. *Elec. J.* 20, 27-30(1923); 9 illus.

C. G. F.

Tungsten lamp manufacture at the Dalston Works. ANON. *Illum. Eng. (London)* 15, 154-7(1922); 4 illus.—Brief description of the process of making W filaments and W incandescent lamps.

C. G. F.

Research and industry. ANON. *Electrician* 90, 222-4(1923).—An illus. description of the new research laboratories of the British Gen. Elec. Co.

C. G. F.

Efficiency of overlapping joints in copper and aluminium busbar conductors. S. W. WILSON. *J. Inst. Elec. Eng. (London)* 60, 889-99(1922).

C. G. F.

Volt-ampere meters. R. C. FRYER. *J. Am. Inst. Elec. Eng.* 42, 123-6(1923).—F. describes different makes of volt-ampere meters and points out the growing necessity for metering on a volt-ampere rather than a watt basis.

W. E. RUNNER

PIÉREARD, E.: *Principes d'électrotechnie*. Vol. 3. 3rd Ed. Paris: Dunod. 330 pp. Fr. 26.

SWIERSTRA, R.: *Electro-Lichttechniek*. Amsterdam: N. V. Mantgem en De Doos. Fl. 4.90. Reviewed in *Arch. Suikerind.* 31, 13(1923).

Dry cell electric battery. G. L. and G. J. A. FULLER. U. S. 1,445,503, Feb. 13. Batteries of no appreciable voltage when in dry condition are formed by use of an electrolyte of pre-dried NH_4Cl or other excitant material of less hygroscopic character than ZnCl_2 , mixed with a pre-dried gum such as gum tragacanth or tapioca.

Electrodes of an aluminium magnesium alloy. F. E. BEIDLER. U. S. 1,446,029, Feb. 20. An alloy of Al 97, Mg 2 and Si and Fe 1 part is used for electrodes for H_2O -softening app., etc.

Calcium carbide. J. H. REID. U. S. 1,445,611, Feb. 20. A charge for carbide production is formed of CaCO_3 particles which are coated and impregnated with coked residue of powdered bituminous coal.

Production of carbide, gas and caustic alkali. J. H. REID. U. S. 1,445,645, Feb. 20. A mixt. of bituminous coal and Na or K feldspar is heated to about $765-1540^\circ$ in a closed retort, the solid product thus formed is further heated in an elec. furnace to produce Al carbide or oxy-carbide or SiC_2 and the gas evolved is scrubbed with H_2O to recover NaOH or KOH sep. from CO and other gas.

Electrolytic production of hydrogen and oxygen. F. G. CLARK. U. S. 1,446,736, Feb. 27. A current is passed between electrodes of permeable material, e. g., wire mesh, immersed in a 17% soln. of NaOH or other suitable aq. electrolyte to produce H and O. A current d. of over 1 amp. per sq. in. of cross section of the current path between the electrodes is maintained and the temp. of the electrolyte is kept above 50° . The permeable electrodes are sep. by a porous diaphragm and are arranged to permit circulation of the electrolyte on both sides.

Electric precipitation of suspended particles from gases. G. A. WITTE. U. S. 1,446,778, Feb. 27. Material (such as C or soot of smoke) which is suspended in gases and tends to form a light flocculent deposit is sep. after addition to the gases of clay, sand, earth or other granular solid weighting material which facilitates elec. pptn. of a compact, heavy, granular deposit.

Electric tilting arc furnace for melting and refining metals. J. S. TUREK. U. S. 1,445,860, Feb. 20. The pat. relates to the construction of the shell and lining.

5—PHOTOGRAPHY

LOUIS DERR

Recent advances in photographic theory. C. E. K. MEES. *J. Franklin Inst.* 195, 1-21(1923).—Review. JOSEPH S. HEBURN

The action of colloids on silver bromide emulsions. ROBERT SCHWARTZ AND HEINRICH STOCK. *Z. wiss. Phot.* 22, 26-32(1922).—The Br liberated by illumination of AgBr can be carried off in a current of air and detd. by absorption in a KI soln. Its variations with the intensity of illumination are proportional to the blackening produced in the AgBr, whether the latter is a pure or a com. gelatin emulsion. The changes produced by light are influenced by the presence of other colloids in the AgBr gel, Pt acting to diminish their speed and oxides and Ag to accelerate it. C. R. FONDA

Study of threshold values of photographic plates by counting grains. W. NODDACK, F. STREUBER AND H. SCHEFFERS. *Sitz. preuss. Akad. Wiss.* 1922, 210-3.—According to the quantum theory one quantum falling upon a AgBr grain splits off one Ag atom, which stays associated with the remaining AgBr; and the latent image, composed of Ag-AgBr grains, is thus made developable. As additional impacts do not sensibly affect the developability, the increase in the number of these developable

grains becomes slower and slower with increasing exposure, as should be expected. The probability of a single grain being struck more than once evidently increases with the grain size, and this is an explanation of the slow increase of blackening (long scale) of fast (coarse-grained) plates as compared with the quick increase (short scale) of slow (fine-grained) plates.

L. DERR

Quantity of light energy required to render developable a grain of silver bromide. P. S. HELMICK. *J. Opt. Soc. Am.* 6, 998-1015(1922).—In the abstract in *C. A.* 17, 497 the expression "2.3 quanta" should read " 2.3×10^6 quanta."

R. J. C.

Effect of dyes in the process of development. R. E. LIESEGANG. *Phot. Ind.* 1922, 601.—The acceleration of development by adding certain basic dyes to hydroquinone developer contg. sulfite, and the absence of effect when no sulfite is present are discussed on the assumption of 2 phys. different forms of Ag, one voluminous and disperse, the other compact and nonporous. The dyes hinder the formation of the latter and thus development can proceed rapidly through the grains; sulfite tends toward the production of a layer of the nonporous form, covering the other and retarding development.

L. DERR

Factors which determine gamma-infinity. G. I. HIGSON AND F. C. TOY. *Phot. J.* 63, 68-74(1923).—Factors, which affect the development factor (slope of the straight portion of the exposure-density curve), partly neutralize one another, and are as follows: wt. of Ag per unit area, its effective sp. gr., size of grains, ratio of gelatin to Ag, wt. of halide per unit area, variation of halide grain size and size of halide grain. A high gamma (3.5-4) corresponds with small grains of uniform size, a low gamma (less than 1.5) to large grains of uneven sizes, a medium gamma (1.5-3.5) to large uniform grains, small uneven grains, or medium-sized grains neither uniform nor very uneven. The behavior of a plate in this respect can usually be predicted from examn. of the unexposed grains.

L. DERR

Influence of adsorbed ions on the photochemical sensitiveness of AgBr (FAJANS, FRANKENBURGER) 3.

Multicolor screen for photography. I. KITSEE. U. S. 1,446,049, Feb. 20. A celluloid film is coated with dichromated gelatin, markings are produced on the coating by the action of light and colored green, the exposed celluloid is tinted with another color (*e. g.*, with a red dye dissolved in a mixt. of acetone and CCl_4 or CH_2O), the surface of the gelatin and celluloid is then covered with varnish, part of the latter is removed in spaced lines and the exposed portions left by its removal are tinted with a third color (*e. g.*, blue). U. S. 1,446,050 relates to the production of multicolor screens by applying to the celluloid film directly 2 different dye solns., one of which, *e. g.*, a dye soln. in acetone and CCl_4 , has a dissolving action on the celluloid and the second of which, *e. g.*, a dye soln. in alc. contg. Peru or Canada balsam, merely adheres to the surface of the celluloid.

Light-sensitized copying paper. G. KÖGEL and H. NEUENHAUS. U. S. 1,444,469, Feb. 6. 1-Diazo-2-hydroxynaphthalene-4-sulfonic acid or similar diazo compd. is used as sensitizing agent on paper, glass or other transparent material. When exposed to light under a photographic negative it is decomposed so that it no longer couples with azo dye components where exposed to light. On treatment of the exposed picture with alkali and a second dye component, *e. g.*, resorcinol, a red or violet picture is obtained. The resorcinol or other second color component may be included in the sensitizing material which may be stabilized by tartaric or citric acid and developed after exposure by the action of NH_3 fumes or other alkali. Phloroglucinol or methylphenylpyrazolone may be used as second components. Cu and Ni salts improve the fastness to light of the

pictures and Fe and Mn salts may be used to regulate their color. After exposure, the pictures may be developed, without use of reagents, by storage in the dark for some time.

Recovering precious metals from photographic fixing baths. B. THOMAS. U. S. 1,446,405, Feb. 20. Fixing baths contg. Ag compds. are regenerated to form $\text{Na}_2\text{S}_2\text{O}_3$ and the precious metals recovered by adding a pptg. agent such as Na_2S and sepg. the ppt. immediately.

6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

Rare earths and their metals. JOHN MISSENDEN. *Chem. News* 126, 51-5(1923).—A review of the history and mineralogical occurrence of the rare earths. M. O. LAMAR

Rare earths. XIV. Preparation and properties of metallic lanthanum. H. C. KREMER and R. G. STEVENS. *J. Am. Chem. Soc.* 45, 614-7(1923).—Fused LaCl_3 with addn. of NaCl and KF was electrolyzed with a current of 40-50 amp. at 7-8 v. Metal prepd. in Fe cells contained up to 15% Fe. With an insulated W rod projecting through the bottom of an Fe cell the metal contained no W and only 0.77% Fe. With graphite cells much carbide was formed. The product was purified by washing with water and melting under pure CaCl_2 . It m. sharply at 826° ; $d_{15} = 6.1598$; Brinell hardness (500 kg. wt.), 37; heat of combustion, 1645 cal. per g.; kindling temp., 445° . The metal is tin-white when freshly filed but tarnishes very rapidly even in dry air. It is not ductile and but slightly malleable. It is not pyrophoric. Alloys with Fe are harder than the metal and are not pyrophoric.

A. R. M.

Cobaltinitrites of bismuth and cadmium. S. C. OGBURN, JR. *J. Am. Chem. Soc.* 45, 641-5(1923).—To a satd. soln. of $\text{Na}_2\text{Co}(\text{NO}_2)_6$ a satd. soln. of $\text{Bi}(\text{NO}_3)_3$ was added, drop by drop without shaking and the ppt. filtered after 1 min. The product was found by analysis to be $(\text{BiO})_2\text{Co}(\text{NO}_2)_6$, color orange. Addn. of more $\text{Bi}(\text{NO}_3)_3$ to the filtrate gave yellow $(\text{BiO})_2\text{Co}(\text{NO}_2)_6$. To the filtrate from this more $\text{Bi}(\text{NO}_3)_3$ was added and after diln. and standing a brick-red ppt. of $(\text{BiO})_2\text{Co}(\text{NO}_2)_6$ was obtained. These compds. decompose on standing and are very hygroscopic. The coordination formulas $[\text{Co}(\text{NO}_2)_4] \cdot 3\text{BiO}$, $[\text{Co}(\text{NO}_2)_4\text{BiO}] \cdot 2\text{BiO}$ and $[\text{Co}(\text{NO}_2)_4(\text{BiO})_2] \cdot \text{BiO}$ are suggested. Satd. solns. of $\text{Na}_2\text{Co}(\text{NO}_2)_6$ and CdSO_4 were mixed and subjected to fractional crystn. at 60° . The bright yellow product corresponded on analysis to $\text{Cd}_3\text{Co}(\text{NO}_2)_6$. It is slightly sol. in cold water and largely sol. in hot water. It decompd. when heated to $175-80^\circ$ and was decompd. by acids, alkalis, and most org. solvents. It is quite stable in aq. soln.

A. R. MIDDLETON

Topochemical reactions. Formation conditions of the varieties of lead oxide. V. KOHLSCHÜTTER and H. ROESY. *Ber.* 56B, 275-88(1923); cf. *C. A.* 16, 523.—Pptn. reactions were studied usually at 15° ; 2 cc. 2 N $\text{Ph}(\text{AcO})_2$ was added to 100 cc. NH_4 soln., 2-12 N contg., in some cases, small concns. of NaOH . Direct and relatively rapid sepn. gave $3\text{PbO} \cdot \text{H}_2\text{O}$ in colloiddally dispersed, flocculent or clearly cryst. form; slower sepn. gave yellow $\text{PbO}(\text{PbO}_2)$ always well crystd. Formation of red $\text{PhO}(\text{PbO}_2)$ was never direct but followed that of hydrate. Cryst. hydrate at ordinary temp. did not change to PbO_2 ; pseudomorphs of the hydrate were formed only at 100° . Colloidal or flocculent hydrate gave PhO_2 as a granular dispersed transformation product which thus seems to require a definite degree of dispersion for its formation. Hydrate was not observed to give PhO_2 from any degree of dispersion. In oxidation of Ph by O_2 in CO_2 -free water cryst. hydrate and PbO_2 are formed and only a little PbO , which forms from suitably dispersed hydrate deposited on the Ph surface. Small addn. of NaOH largely increases hydrate and causes it to assume a more compact form; PhO_2 is much decreased,

PbO, wholly suppressed. Crystals of PbCl_2 in NaOH , 5–10 *N*, were changed to PbO , completely but the cryst. form remained unchanged. PbSO_4 in 10 *N* NaOH changed completely to PbO , in well formed rhombic crystals; no pseudomorphs were observed. $3\text{PbO} \cdot \text{H}_2\text{O}$ well crystd. changed at 110° to pseudomorphs of PbO , and these at 650° to PbO , without change of form but contraction took place, probably because of sintering of the originally highly dispersed material of the pseudomorphs. This accounts for the uniformly greater density found for PbO , by other observers. PbCO_3 heated in air at 400° gave a red product not Pb_3O_4 ; both this and basic carbonate heated in N_2 at 450° gave a red oxide of similar appearance; both changed into PbO , at 650° without change of form. Oxidation of Pb vapor gave highly dispersed PbO , in which the cryst. form could not be distinguished. It is concluded that PbO , forms only from mol. soln. or dispersion while for PbO_2 a definite degree of dispersion is requisite which permits contraction and thus gives rise to a distinct topochemical factor. Where both oxides form from soln. anhydride formation results from amphoterism of $\text{Pb}(\text{OH})_2$, as in $\text{Cu}(\text{OH})_2$ (cf. Euler and Euler, *C. A.* 17, 504), and $\text{Pb}(\text{OH})_2 \rightarrow \text{PbO} + \text{H}^+ + \text{OH}^-$ may form PbO ; by condensation of several mols. of hydrate, $2\text{PbO} \cdot \text{Pb}(\text{OH})_2$, or red oxide, (3PbO) , may result. It is noteworthy that in spontaneous transformation of hydrate the topochemical conditions cause the exclusion of PbO_2 , which energetically stands nearer the hydrate, in favor of the more remote PbO , contrary to the law of stages. This example must have wider significance particularly for certain reactions of org. chemistry.

A. R. MIDDLETON

A class of unstable hydrates called hydrates of gas. A. BOUZAT. *Compt. rend.* 176, 253–5(1923).—From their dissociation curves, B. has calcd. the compn. of the hydrates of Cl, Br and SO_2 . These conform to the formula $\text{M} \cdot 6\text{H}_2\text{O}$. In general these hydrates are characterized by their instability and low heat of formation. A consideration of the large number of unstable hydrates of the formula $\text{M} \cdot 6\text{H}_2\text{O}$ indicates the presence in water of $(\text{H}_2\text{O})_4$ mols. or at least of $(\text{H}_2\text{O})_n$ mols., where n is 3 or a multiple of 3.

L. T. FAIRHALL

Hydrates of krypton and argon. R. DE FORCRAND. *Compt. rend.* 176, 355–8(1923).—F. confirms the existence of a hydrate of A reported by Villard in *Compt. rend.* 123, 377(1896). He reports in addition a hydrate of Kr. For $\text{A} \cdot (\text{H}_2\text{O})_n$, $n = 5.14$ – 5.50 at 8° ; the vapor pressure between 0.0° and $0.4^\circ = 98.5$ atm.; at $8^\circ = 210$ atm.; the calcd. heat of formation is 14.855 Cal. For $\text{Kr} \cdot (\text{H}_2\text{O})_n$, $n = 5.08$; the vapor pressure at $0^\circ = 14.5$ atm., at $4.8^\circ = 23.5$ atm., at $10.3^\circ = 38.7$ atm., at $12.5^\circ = 47.5$ atm.; the calcd. heat of formation between 0° and 12° is 14.712 Cal.; the critical point of decompn. is 12.5 – 13° (75° above the critical temp. of Kr). The other rare gases should form hydrates and the stability of these hydrates should increase with increasing at. wt.

F. E. BROWN

Active chlorine. Y. VENKATARAMAIAH. *J. Phys. Chem.* 27, 74–80(1923).—Pure Cl was prepd. by heating purified AuCl_3 . The Cl activated by (1) silent elec. discharge, (2) elec. discharge, (3) ultra-violet light, and (4) beat was more active than ordinary Cl. It combines with ozone to form Cl_2O , S to form S_2Cl_2 , Te to form TeCl_4 , etc. When Cl is activated it contracts in vol. Active Cl is unstable and is decomposed above 50° . V. concludes that an allotropic form of Cl is produced.

L. T. FAIRHALL

Catalytic decomposition of hexamminocobalt chloride. ROBT. SCHWARZ AND W. KRÖNIG. *Ber.* 56B, 208–14(1923); cf. *C. A.* 15, 3950.—An error was inherent in the analytical methods of the earlier work and Co values were too high. $\text{Co} \cdot \text{NH}_3$ is the same in products and starting substances; SiO_2 does not enter the complex but silicates are formed. Compds. previously formulated are to be stricken out. However, H_2SiO_3 gels catalyze the decompn. $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 = [\text{Co}(\text{NH}_3)_4\text{Cl}]\text{Cl}_2 + \text{NH}_3$ upon prolonged shaking. Carbon acts similarly; it was employed in the forms "Kohle A" (Bayer)

and "Sanasorbe." Both Co and NH_3 are adsorbed but evidence is presented that not the complex but $\text{Co}(\text{OH})_2$ and NH_3 are the adsorbed mols., formed according to $[\text{Co}(\text{NH}_3)_6]\text{Cl} + 3\text{H}_2\text{O} = \text{Co}(\text{OH})_2 + 3\text{NH}_4\text{Cl} + 3\text{NH}_3$. Max. formation of purpureo chloride takes place in 1% soln. of luteo chloride. Larger amts. of carbon decolorize the 0.5% soln. completely and all the Co is adsorbed; for higher concns. the amt. of purpureo salt is independent of the concn. and proportional only to the amt. of carbon.

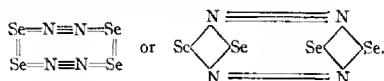
A. R. MIDDLETON

Cuprous sulfites. V. V. SARMA. *Chem. News* 126, 61-2(1923).—By satg. with SO_2 a weak NaOH or KOH soln. in which is suspended yellow Cu_2O is prepd. a basic cuprous sulfite, a bright red granular ppt. of sp. gr. 3.26. Heated in a test-tube it loses H_2O and SO_2 , becoming successively yellow, red and black; in the air beyond 145° it leaves a residue which contains CuSO_4 and Cu_2O ; it is hydrolyzed by hot H_2O , forming CuSO_4 and Cu_2O . With dil. HCl, SO_2 is evolved and Cu_2Cl_2 formed. Dil. alkalis give a ppt. of yellow Cu_2O and a pale blue soln. contg. alkali sulfite but no $\text{Cu}(\text{OH})_2$. The formula $\text{Cu}(\text{Cu}_2\text{O} \cdot 0.4\text{H}_2\text{O})\text{SO}_3 \cdot \text{H}_2\text{O}$ is proposed.

M. O. LAMAR

Selenium nitride. W. STRECKER AND L. CLAUS. *Ber.* 56B, 362-83(1923).—Liquid NH_3 reacted vigorously with Se_2Cl_4 or Se_2Br_4 with sepn. of red Se. From solns. of the former in CHCl_3 or dry C_6H_6 only traces of nitride were sometimes observed in the red Se. Solns. in Et_2O at -80° formed with NH_3 much red Se and a colorless liquid which became bright yellow during removal of Et_2O and excess NH_3 and deposited bright-brown Se_2NCl and $\text{Se}_2\text{N}_2\text{Br}$. SeOCl_2 in Et_2O soln. in open vessels formed white $\text{SeOCl}_2 \cdot 4\text{NH}_3$, decompd. by water to Se and SeN; in a closed tube SeOCl_2 and excess of NH_3 were maintained 3 days at room temp. then at 50° for 2 hrs. The tube was cooled in Et_2O -solid CO_2 ; explosion was caused by opening but most of the product, chiefly SeN, was saved. Solid SeCl_4 and SeBr_4 react violently with liquid NH_3 with sepn. of Se; in CS_2 suspension SeCl_4 becomes deep green, the color vanishing on evapn. of NH_3 ; the product is a yellow-white amorphous powder, instantly decompd. by water with sepn. of Se and a little SeH_2 , which could not be obtained pure. SeBr_4 in CS_2 soln. reacts less vigorously than SeCl_4 and gives SeN purer and in better yield than Verneuil's method (*Bull. soc. chim.* [2] 38, 548(1882)). The reaction is not that found by V. for SeCl_4 but corresponds to $3\text{SeBr}_4 + 16\text{NH}_3 = 2\text{SeN} + \text{Se} + \text{N}_2 + 12\text{NH}_4\text{Br}$. SeN is best prepd. by leading dry cold NH_3 gas into a soln. of 5 g. SeBr_4 in 500 cc. absolutely dry CS_2 in a 1-l. Erlenmeyer flask cooled by ice-salt and protected by a soda-lime tube. The ppt. of SeN, NH_4Cl and Se is filtered, washed with CS_2 , placed in a flask, CS_2 removed by dry air, NH_4Cl by water and Se by refluxing with CS_2 and the product dried in air or over H_2SO_4 . As solvent for SeBr_4 dry C_6H_6 may be used and NH_3 admitted at $5-10^\circ$. SeN forms a bright-orange powder, extremely explosive when dry and its instability increases with its degree of purity. It must be kept in cardboard and not in glass as friction of a stopper upon a particle may cause violent detonation. Analysis was by explosion in a special vacuum app. (pictured) and measuring N_2 evolved. Explosion temp. was 160° . A dil. soln. of Br_2 in CS_2 was added to a suspension of SeN in CS_2 and allowed to react 5 days, more Br_2 being added on days 2 and 3; the color became successively yellow, brown, red and the product finally assumed a uniformly dark color; after washing with CS_2 and drying *in vacuo* it formed a brown-green powder, deliquescent in air, decompd. instantly by water with sepn. of Se, sol. in concd. HNO_3 with decompn., with NaOH gives Se and NH_3 . Analysis indicated the formula SeN_2Br_4 . Br vapor detonates dry SeN but by slow action. In an atm. of CO_2 reaction was begun on several 10-mg. portions for 1 hr. and then continued 4 days in pure Br vapor; the product was first liquid then formed a deep-red powder, which was washed with CS_2 and recrystd. from concd. HBr in deep-red crystals identical with Muthmann's $(\text{NH}_4)_2\text{SeBr}_4$. Under similar conditions Cl_2 much dild. with CO_2

forms a mixt. which can be exposed to an atm. of Cl_2 and reaches const. wt. in 2 days. The product is bright rose-brown, fairly stable in air, decompd. by water to Se , H_2SeO_3 and HCl . Analysis indicated the formula SeNCl_3 . Under similar procedure Br_2 with $\text{Se}_2\text{N}_2\text{Br}$ formed $(\text{NH}_4)_2\text{SeBr}_6$. SeN did not react with solid I or in Et_2O or CHCl_3 soln. but exploded on contact with fused I . Mol. wt. detn. was impossible as no solvent could be found. A suspension of NaN_3 in C_6H_6 was boiled with reflux and a soln. of SeOCl_2 in C_6H_6 added dropwise. The N_2 evolved was measured and corresponded to about 0.5 that of the NaN_3 . The product was $2\text{NaCl} \cdot \text{SeO}_2 \cdot 11\text{H}_2\text{O}$. It is concluded from this and other expts. with Se halides and AgN_3 that SeN is not comparable to an azide of Se . If the formula Se_2N_4 is assumed, in analogy with S_2N_4 , the reactions of the nitride are in accord with a structure such as



A. R. MIDDLETON

Hydrogen hexasulfide and the solubility of sulfur in the persulfides of hydrogen. J. H. WALTON AND E. L. WHITFORD. *J. Am. Chem. Soc.* 45, 601-6(1923).— S dissolves copiously in both H_2S_2 and H_2S_6 , the resulting liquid phases having the same compn. at the same temp. The soly. curve for S in H_2S_2 has been established between -34.71° and $+55.3^\circ$. A compd., H_2S_6 , stable below -1.45° , has been found to exist.

H. JERMAIN CREIGHTON

Silicon hydrides. XII. Disiloxane, $(\text{SiH}_3)_2\text{O}$. ALFRED STOCK AND CARL SOMESKI. *Ber.* 56B, 132-5(1923); cf. *C. A.* 14, 1494-2305.—Prepn. of disilene, Si_2H_4 , by removal of water from $(\text{SiH}_3)_2\text{O}$ proved impossible. Action of SiH_3Cl on $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ or $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ gave no better yield of disiloxane than previous methods. Heating decompd. disiloxane only slightly after 0.5 hr. at 400° ; this is a new proof of the great stability of the chain: $\text{Si} \cdot \text{O} \cdot \text{Si}$. Slightly moist P_2O_5 at room temp. completely decompd. disiloxane after several days; dry P_2O_5 was without effect. The products were little H_2 , much SiH_4 and polymers of prosiloxane, $\text{SiH}_2(\text{O})$. Traces of water start $(\text{SiH}_3)_2\text{O} + \text{H}_2\text{O} = 2\text{SiH}_2(\text{O}) + 2\text{H}_2$; then $(\text{SiH}_3)_2\text{O} + 2\text{H}_2 = 2\text{SiH}_4 + \text{H}_2\text{O}$ and water thus formed catalyzes $(\text{SiH}_3)_2\text{O} \rightarrow \text{SiH}_4 + [\text{SiH}_2(\text{O})]_x$. This series of reactions probably occurs in decompn. of disiloxane by heat and accounts for the poor yields in its prepn. A similar catalytic action of NH_3 is probable in the spontaneous decompn. of $(\text{SiH}_3)_2\text{NH}$ at room temp. and of water in decompn. by heat of $(\text{SiCl}_3)_2\text{O} \rightarrow \text{SiCl}_4 + [\text{SiCl}_2(\text{O})]_x$. **XIII. Reactions of chloromonosilane and disilane.** *Ibid* 247-52.—Decompn. of SiH_3H by heat began at 350° and was rapid at 400° and 500° . Products were little Si , much H_2 and SiH_4 ; also at 400° small amts. of higher hydrides. A volatile Si-CN compd. could not be obtained from SiH_3Cl and AgCN ; there was only a trace of reaction in 48 hrs. at room temp.; after 24 hrs. at 150° all of 12.9 cc. of SiH_3Cl reacted and 5 cc. HCN and 15.5 cc. $(\text{CN})_2$ were found. H_2S did not react with SiH_3Cl at room temp.; in the presence of AlCl_3 after several days at 150° a volatile S compd. not yet investigated was formed. Probable reactions are $\text{SiH}_3\text{Cl} + \text{H}_2\text{S} = \text{SiH}_4(\text{SH}) + \text{HCl}$ and $\text{SiH}_3\text{Cl} + \text{HCl} = \text{SiH}_2\text{Cl}_2 + \text{H}_2$. Prolonged treatment of very pure SiH_2Cl_2 with dil. Na-Hg gave a yellow solid product which from its reactions, particularly strong luminescence in contact with KMnO_4 crystals under HCl (cf. Kautzky, *C. A.* 15, 3796), probably contains strongly unsatd., highly condensed Si hydrides. Probable reactions are $\text{SiH}_2\text{Cl}_2 + 4\text{Na} = \text{SiH}_2\text{Na}_2 + 2\text{NaCl}$; $\text{SiH}_2\text{Na}_2 + \text{Hg} = \text{SiH}_2 + \text{Na-Hg}$; $3\text{SiH}_2 \rightarrow \text{SiH}_4 + 2(\text{SiH})_2$. These are complicated by side reactions. A. R. MIDDLETON

Mechanism of the reaction in the formation of silicane from magnesium silicide. I. ROBERT SCHWARZ AND ERICH KONRAD. *Ber.* 55B, 3242-52(1922).—In the reaction

between Mg_2Si and HCl , only a few % of the Si appears as SiH_4 . A large no. of expts. on Mg_2Si , freed from Mg by Grignard's reaction, showed that at 0° after 30 hrs. the silicide had been completely decompd. and the resulting white solid corresponded to the formula $H_2Si_2O_4$ and had the properties of *dioxodisiloxan*. In aq. solns. the Mg goes into soln. as $MgCl_2$ and is present only in traces in the solid residue, but in decompns. with alc. HCl about 20% of the Mg remains and does not wash out with in-

creased amts. of HCl and alc. The reaction is probably,
$$\begin{matrix} & Mg \\ & \diagup \quad \diagdown \\ HO.Mg & Si & + 2HOH = \\ & \diagdown \quad \diagup \\ HO.Mg & \end{matrix}$$

$HO.Mg \gg SiH_4$ (A). Only 15% of the Si is present in the solid and no SiH_4 is evolved.

The remaining 85% of the Si is in the clear alc. filtrate as an *alcosol*, of silicic acid. Accordingly, a reaction similar to the following probably takes place: $Mg_2Si + 4HCl + 2H_2O = 4H_2 + 2MgCl_2 + SiO_2$. A no. of expts. in which the alc. content was varied showed only that the formation of SiH_4 increased with alc. content. It is therefore assumed that the primary product of hydrolysis, A, reacts as follows: $A + 2HOH = 2Mg(OH)_2 + SiH_4$. It is possible that the following reaction may also take place. $A + H_2O + 4HCl = 2MgCl_2 + 2H_2O + SiH_2O + 2H_2$. D. MACRAE

Reduction of potassium chlorate by ferrous sulfate. M. HERSCHKOWITSCH. Z. anorg. allgem. Chem. 125, 147-54 (1923).—This investigation was undertaken to account for vigorous evolution of Cl_2 from a mixt. of 500 kg. $KClO_3$ and 500 kg. $FeSO_4$ supposed to be anhydrous. Both salts had been analyzed some time before mixing and found pure. It was found that a perfectly dry mixt. of the salts can be warmed to 100° without reaction. Contrary to the literature, in presence of small amts. of water ClO_2 and Cl_2 are formed. The reaction proceeds through formation of $Fe_2(SO_4)_3$, $FeCl_3$ and free HCl which reacts with more $KClO_3$. ClO_2 and Cl_2 were found to be formed in approx. equal amts. In the presence of large amts. of water chlorate was found to be reduced completely to chloride. A. R. M.

Systematic affinity principle. XIX. Amines of barium halides. G. F. HÜRTIG AND W. MARTIN. Z. anorg. allgem. Chem. 125, 269-80 (1923); cf. C. A. 17, 499.—Stable compds. found (italicized ones are new), min. and max. p_{NH_3} measured, and Q values calcd. from the Nernst equation were as follows: $BaCl_2.8NH_3$, 189 mm. at -15.5° , 500 mm. at 0° , 9.0 Cal. $BaBr_2.8NH_3$, 70 mm. at 0° , 641 mm. at 33° , 10.0 Cal. $BaBr_2.4NH_3$, 49 mm. at 0° , 497 mm. at 33° , 10.2 Cal. $BaBr_2.2NH_3$, 25 mm. at 0° , 219 mm., at 33° , 10.6 Cal. $BaBr_2.NH_3$, 5 mm. at 0° , 37 mm. at 41° , 11.8 Cal. $BaI_2.10NH_3$, 18 mm. at -78° , above 844 mm. at 0° , 7.7 Cal. $BaI_2.9NH_3$, 137 mm. at 0° , 430 mm. at 33° , 10.0 Cal. $BaI_2.8NH_3$, 23 mm. at 0° , 195 mm. at 33° , 10.7 Cal. $BaI_2.6NH_3$, 14 mm. at 0° , 100 mm. at 33° , 11.1 Cal. $BaI_2.4NH_3$, 70 mm. at 33° , 335 mm. at 63° , 11.3 Cal. $BaI_2.2NH_3$, 16 mm. at 63° , 54 mm. at 78° , 13.4 Cal. The temps. at which $p_{NH_3} = 100$ mm. are: $BaCl_2.8NH_3$, -23° ; $BaBr_2.8NH_3$, $+4^\circ$, $4NH_3$, 9.5° , $2NH_3$, 20° , $1NH_3$, 53° ; $BaI_2.10NH_3$, -58° , $9NH_3$, $+4^\circ$, $8NH_3$, 23° , $6NH_3$, 34° , $4NH_3$, 39° , $2NH_3$, 97° . A. R. MIDDLETON

Hydrocyanic acid: an ammonocarbonous acid, and ammonoformaldehyde and a formic anammonide. E. C. FRANKLIN. J. Phys. Chem. 27, 167-86 (1923).—The theoretically possible $C(OH)_2$ and $C(NH_2)_2$ may be written, resp., as an aquo- and an ammono-carbonous acid. As CO would thus be the anhydride of the unknown carbonous acid, so removal of NH_3 from the hypothetical ammonocarbonous acid and from formimidine, $H C(NH)NH_2$, which is formally an ammonoformic acid, would leave $H-N \equiv C$, ammonocarbonous acid, and $H-C \equiv N$, an ammonoformaldehyde and at the same time a formic anammonide. Many familiar and some new reactions are interpreted in accordance with this view. That HNC is ammonocarbonous acid: (1)

its formation when C is heated with N_2 and H_2 or with NH_3 ; (2) conversion of NaNC by N_2 in presence of Na into Na_2CN_2 ; (3) formation of Na_2CN_2 by action of NaN_3 on fused NaNC; (4) formation of Na dicyanide from NaNC and C_2N_4 ; (5) at $350-400^\circ$ $2NaNH_2 + C = Na_2CN_2 + 2H_2$ (nitridation of C to ammonocarbonite) and at higher temp. $Na_2CN_2 + C = 2NaNC$ (reduction to ammonocarbonite), also the reactions $2NaNH_2 + CO = NaNC + NaOH + NH_3$ and $6NaNH_2 + 3CO_2 = Na_2CN_2 + 2Na_2CO_3 + 4NH_3$; (6) reduction of Na_2CN_2 and of $NaN(CN)_2$ to NaNC; (7) oxidation of NaNC to NaNCO; (8) ammonolysis of ethylcarhylamine according to $EtNC + KNH_2 = EtNH_2 + KNC$; (9) oxidation of methylcarhylamine to the isocyanate according to $MeNC + HgO = MeNCO + Hg$ and at 130° $MeNC + S = MeNCS$; (10) reduction of HNC to $MeNH_2$. In favor of the view that $H-C\equiv N$ is an ammono-formaldehyde are: (1) its ready polymerization; (2) condensation to aldol-like products; (3) formation of addn. compds. with acid sulites; (4) reacts like HCHO with H_2NOH , N_2H_4 and PhN_2H_2 ; (5) the relation to $MeNH_2$ as that of an aldehyde to an alc. as shown by the easy reducibility of HCN to $MeNH_2$ and ready oxidation of the latter to HCN. The relation of HCN to formamide, formamidine and the formimido esters, resp., is shown to be analogous to that of acid anhydrides to the acids. A. R. M.

Higher oxide of cobalt. O. R. HOWELL. *J. Chem. Soc.* 123, 65-71 (1923).—The action on $CoSO_4$ of (1) NaOH and NaClO and (2) CaO and bleaching powder was studied. The conclusions reached are: (1) Hypochlorites free from alk. ppt. a slightly peroxidized sesquioxide of const. compn. and about 1.05 equivs. of available O. Pptn. is far from quant. apparently because the peroxide catalytically decomps. hypochlorite. (2) When less than 0.5 equiv. of hypochlorite is used with excess of alk., more available O is found in the ppt. than was used from the hypochlorite; this is attributed to atm. oxidation of the ppt. (3) A higher degree of oxidation is reached with hypochlorite and alkali than with the former alone. This is attributed to direct oxidation of $Co(OH)_2$ to a peroxide such as $CoO(OH)_2$. (4) Temp. and concn. are practically without influence on the compn. of the ppt. The peroxide is very stable, loses no available O on prolonged boiling and can be kept indefinitely. A. R. M.

Complex phosphato- and arsenatometal acids. I. DEDE. *Z. anorg. allgem. Chem.* 125, 28-46 (1923).—Solns. of ferric, Al and Be salts when mixed with solns. of H_3PO_4 and H_3AsO_4 showed much higher sp. conds. than the sum of the sep. conds. of salt and acid. The cond. curves rose sharply at first; with ferric salts this sharp rise ended when 1 equiv. of acid was added to 1 equiv. of Fe. The data indicated existence of complex acids such as $H_2[Cl_2FePO_4]$ but these could not be isolated. On further addn. of acid these complexes formed $H_2[Fe(PO_4)_2] \cdot 2.5H_2O$ and $H_2[Fe(AsO_4)_2] \cdot xH_2O$ which were isolated and analyzed. Through this formation of complexes the oxidizing action of ferric ion and of H_3AsO_4 is strongly repressed or completely annulled. The complexes of Al and Be were much less stable. Evidence was obtained for a similar complex formation with Mn^{III} but not with Cr. A. R. M.

Polythionic acids. F. FOERSTER AND A. HORNIG. *Z. anorg. allgem. Chem.* 125, 86-146 (1923).—The work of earlier investigators was checked, more modern methods being used. Action of H_2S on SO_2 in aq. soln. gives primarily a product, probably $H_2S_2O_6$, in equil. with the reacting substances and which reacts with H_2S to form S and with SO_2 to form $H_2S_2O_6$. Of the polythionic acids and their alkali salts $H_2S_2O_6$ is by far the most stable, $H_2S_3O_6$ the least stable, while $H_2S_4O_6$ is intermediate. The contrary observation of Riesenfeld and Feld (*C. A.* 16, 1714) is due to use of an unsuitable method for detn. of $H_2S_2O_6$. None of these acids or their salts is entirely stable in aq. soln.; they undergo the following transformations: $S_2O_4^{2-} \rightleftharpoons S_2O_4^{2-} + S$; $S_4O_6^{2-} \rightleftharpoons S_2O_4^{2-} + S$; $S_3O_6^{2-} + H_2O \rightleftharpoons SO_4^{2-} + S_2O_4^{2-} + 2H^+$; $S_2O_4^{2-} + H^+ \rightleftharpoons HSO_4^- + S$. The end-products, SO_4^{2-} , SO_2 and S, result in amts. calcd. from these equations only when removal of SO_2

and pptn. of S drive the equil. far toward the right. These conditions are best obtained at b. temp. While $S_2O_4^{2-}$ and H^+ exist only transiently in the soln., a certain portion of them undergoes polymerization, $5S_2O_4^{2-} + 10H^+ \rightarrow 2S_5O_4^{2-} + 4H^+ + 3H_2O$, with the result that $H_2S_2O_4$ and its salts are never smoothly transformed to SO_3^{2-} , SO_2 and S but a certain fraction of them forms higher polythionic acids. The more SO_3 and free S can remain in soln. the more $H_2S_2O_4$ undergoes polymerization and the reactions $S_2O_4^{2-} + S_2O_4^{2-} + H^+ = S_4O_4^{2-} + HSO_3^-$ and $S_2O_4^{2-} + S_2O_4^{2-} + H^+ = S_4O_4^{2-} + HSO_3^-$. At room temp. the conditions are most favorable for $H_2S_2O_4$ to remain in the soln. and the various stages in decompn. of the polythionates become most evident. The overlapping of these processes was established and in part quant. followed. High concn. of H^+ greatly retards decompn. of $H_2S_2O_4$ and $H_2S_2O_6$ but affects little or not at all that of $H_2S_2O_8$. $H_2S_2O_8$ is decompd. by H_2SO_3 to $H_2S_2O_4$ far more rapidly than the latter to $H_2S_2O_4$. Since in the action of H_2S on SO_3 polythionic acids result only when $SO_3:H_2S$ exceeds 1:2 and since the primary product requires time to form $H_2S_2O_8$ with H_2SO_3 there is sufficient time for $H_2S_2O_8$ to form $H_2S_2O_4$ with H_2SO_3 and this action is greater the greater the mol. ratio of $SO_3:H_2S$. The transition of $H_2S_2O_8$ into $H_2S_2O_4$ proceeds so slowly in presence of H_2SO_3 that in the ordinary prepn. of Wackenroder soln. only extremely small concns. of $H_2S_2O_8$ and its decompn. product H_2SO_3 are formed. Larger amts. of these result only after prolonged treatment of the mixt. of $H_2S_2O_8$ and $H_2S_2O_4$ with SO_3 .

A. R. M.

Interaction of carbon tetrachloride and fuming sulfuric acid. A. I. LEPIN. *J. Russ. Phys. Chem. Soc.* 52, 1-17(1920).—L. has investigated the mechanism of the formation of $COCl_2$ and chlorosulfonic acid from CCl_4 and fuming H_2SO_4 (cf. Schützenberger, *Ann.* 154, 375(1870); Armstrong, *J. prakt. Chem.* [ii] 1, 246(1870); Erdmann, *Ber.* 26, 1990-94). If the fuming acid contains 45% of dissolved SO_3 , corresponding with the formula $H_2S_2O_7$, the reaction is expressed by the equation, $CCl_4 + H_2SO_4 \cdot SO_3 = COCl_2 + 2SO_2 \cdot HCl$. If less than 45% of dissolved trioxide is present, so that the acid may be regarded as a soln. of fuming in monohydrated acid, the fuming acid acts as above, the excess of monohydrate remaining together with the secondary product, chlorosulfonic acid. Finally, if the dissolved SO_3 exceeds 45%, the acid may be considered as a mixt. of $H_2S_2O_7$ with SO_3 . In this case, part of the CCl_4 reacts according to the equation $CCl_4 + H_2SO_4 \cdot SO_3 = COCl_2 + 2SO_2 \cdot HCl$, and part according to $CCl_4 + 2SO_3 = COCl_2 + S_2O_3Cl_2$; both these reactions proceed quant.

J. C. S.

Action of silver sulfate in sulfuric acid solution on certain halogen derivatives. E. A. SHILOV. *Bull. Inst. Polyt. Ivanovo-Voznesensk* 4, 169-70(1921).—A soln. of Ag_2SO_4 in concd. H_2SO_4 acts on MeI, EtCl or EtBr, or ethylene bromide more energetically than an alc. soln., of $AgNO_3$ of identical concn. The reaction proceeds in 100% H_2SO_4 but is greatly influenced by the presence of water, the function of which has not yet been explained. With EtBr and a strong H_2SO_4 soln. of Ag_2SO_4 , the products obtained include $AgBr$ and $EtHSO_4$, but not Et_2SO_4 , the latter undergoes only slow conversion into $EtHSO_4$ under the influence of concd. H_2SO_4 and is hence not formed even as an intermediate product. The amount of $EtHSO_4$ separable as Ba salt amounts to only about 77% of the calcd. quantity. Since in the H_2SO_4 soln. the Ag probably exists as the complex ion $AgSO_4^+$, the energetic action on alkyl halides is scarcely compatible with Bruyn and Steger's theory (*Rec. trav. chim.* 18, 41-71, 311-25(1899)) which assumes electrolytic dissociation of the Ag salt and alkyl halide.

J. C. S.

Complex magnesium salts. G. SPACU. *Bull. soc. Stiinta Cluj* 1, 72-91(1921).—A number of complex pyridine compds. of Mg contg. combined water are described. Tetraaquodipyridinemagnesium chloride, $[MgPy_2(H_2O)_4]Cl_2$, is obtained by the action of anhyd. pyridine on carnallite; it crysts. in needles which deliquesce on exposure to air with liberation of pyridine. It gives $Mg(OH)_2$ on treatment with NH_3 , and $AgCl$

with AgNO_3 . *Triaquatripyridinemagnesium chloride*, $[\text{MgPy}_3(\text{H}_2\text{O})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$, is similar to the preceding compd. *Diaquatetrapyridinemagnesium bromide*, $[\text{MgPy}_4(\text{H}_2\text{O})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$, forms very hygroscopic crystals which give up their water of crystn. in a vacuum over P_2O_5 . *Aquopentapyridinemagnesium iodide*, $[\text{MgPy}_5(\text{H}_2\text{O})]\text{I}_2 \cdot 2\text{H}_2\text{O}$, forms crystals from which I seps. on exposure to air; it is less hygroscopic than the preceding compds.: *Tetraaquodipyridinemagnesium nitrate*, $[\text{MgPy}_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, forms nacreous lamellas. The anhyd. salt has similar properties. *Hexapyridinemagnesium bromide*, $[\text{MgPy}_6]\text{Br}_2$, is prepd. by the Tissier-Grignard reaction by way of the ether compd., $[\text{MgPy}_6(\text{Et}_2\text{O})_2]\text{Br}_2$. The latter is a light yellow, unstable powder which gives with anhyd. pyridine at 100° the hexapyridinemagnesium bromide: the latter forms platelets and is very hygroscopic and unstable. *Hexapyridinemagnesium iodide* is similarly prepd. and resembles the corresponding bromide. J. C. S.

BILTZ, E. and BILTZ, G.: *Practicas de quimica inorganica*. Barcelona: Manuel Marin. 292 pp. Pcs. 12.

SCHEID, KARL: *Anorganische Chemie*. 3rd Ed. Leipzig: Quelle & Meyer. 243 pp.

SPENCER, JAMES FRIDERICK: *Les métaux des terres rares*. Paris: Dunod. 280 pp. Fr. 36, bound, Fr. 39.50.

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Report of the committee on editing methods of analysis. R. E. DOOLITTLE, *et al.* *J. Assoc. Official Agr. Chem.* 6, 113-9 (1922).—Changes and additions to the methods of analysis made at the 1920 meeting of the association are given. H. A. LEFER

Standards of purity for analytical reagents. A. KLING and A. LASSIEUR. *Chimie et industrie* 9, 15-25 (1923).—A list of the principal reagents and of the tests to which they should answer to be suitable for general analytic work, comprising: glacial AcOH , As_2O_3 , CrO_3 , citric acid, HF , HCl , HNO_3 (pure and fuming), HClO_4 , H_2SO_4 , tartaric acid, KOH , NaOH , $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, CaO , NH_4OH , K_2CO_3 , Na_2CO_3 (anhyd. and cryst.), NaHCO_3 , $(\text{NH}_4)_2\text{CO}_3$, NH_4Cl , $(\text{NH}_4)_2\text{MoO}_4$, NH_4NO_3 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, NaHSO_4 , NaCl , $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{C}_2\text{O}_4$, KHSO_4 , KClO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, KI , KMnO_4 , $\text{K}_2\text{S}_2\text{O}_8$, CaCO_3 , BaCO_3 , BaCl_2 , ZnO , PbO_2 , AgNO_3 , I , Zn . A. P.-C.

Austrian standards for the chemical analysis of metals. ANON. *Oesterr. Chem. Ztg.* 26, 15-6 (1923).—Provisional methods for (a) sampling ferrous alloys, and (b) analysis of ferro-Si, are offered, with the request that they be subjected to exhaustive trial and criticism. W. C. EBAUGH

The best way to standardize volumetric solutions. F. L. HAHN. *Z. angew. Chem.* 36, 14-5 (1923).—An argument favoring standardizing with sep. weights of standard rather than with aliquot parts of a soln. obtained from a single wt. of substance. W. T. H.

The bimetallic electrode applied to neutralization reactions. H. H. WILLARD and F. FENWICK. *J. Am. Chem. Soc.* 45, 715-6 (1923); cf. *C. A.* 17, 37.—In titrating a 0.1 *N* HCl soln. with 0.1 *N* NaOH using the bimetallic electrode consisting of 2 Pt wires with a polarizing voltage of 0.5 volt through an external resistance of 100,000 ohms, the galvanometer was extremely sluggish in the region of the neutral point. The addition of KBrO_3 did not improve matters but a little neutral H_2O_2 soln. caused a return of the normal sensitivity. Upon adding alkali there was a sharp downward break at the neutral point. With the reversed titration there was an upward break of about 100 millivolts at the neutral point and an excess of acid caused the voltage to

fall. The neutral point indicated corresponded to about $p_H = 6.8$. Evidently the bimetallic electrode system can be sometimes used as a H electrode which is unique because it is independent of an external gas supply. W. T. H.

Some new sulfonephthalein indicators. BARNETT COHEN. *Public Health Repts.* **38**, 199(1923).—A few new sulfonephthalein indicators are suggested for filling in the gaps in the indicator series for the detn. of H-ion concn. by the colorimetric method.

C. R. CARLSON

The Kleemann modification of the Kjeldahl process. FRANTISEK SKUTIL. *Chem. Listy* **16**, 173-7(1922).—The various methods of estg. the N of foodstuffs and fertilizers, using modifications of the Kjeldahl process, are reviewed, and the advantages of the Kleemann modification (C. A. **16**, 1196) pointed out. Results obtained by a modification of this method are found to be in satisfactory agreement with those obtained by the standard analytical method used in Czechoslovakia. This method differs from that of Kleemann in that, after the addn. of Hg, 30% of H_2O_2 is added, and then the concd. H_2SO_4 slowly, and with cooling. After some time, the contents of the flask are heated until a deep coloration appears. Finally, anhyd. K_2SO_4 is added, and the process completed. J. C. S.

Sodium peroxide. JAROSLAV MILBAUER. *Chem. Listy* **16**, 84-6(1922).—The estn. of the active O of Na_2O_2 by means of acid $KMnO_4$ soln. is examd. The best results are obtained by the addn. of boric acid to the soln., as this fixes the H_2O_2 liberated by the acid. This method is very exact and rapid, and does not require the use of ice. The effects produced by the presence of various metallic salts, and of spongy Pt and Pd are also investigated. If the salt is added to the water before the Na_2O_2 , the results for the estn. of O will be low; if the salt is added after the soln. of the Na_2O_2 in water the results are high. This explains the failure of the use of $KMnO_4$ soln. alone, as the $MnSO_4$ formed acts as a catalyst, which must be neutralized by an anti-catalyst (in this case boric acid). The iodometric method of Kuznetz (J. Chem. Soc. **37**, 792(1880)) is also examd. and found satisfactory. The influence of catalysts on the method, whereby the peroxide is analyzed by estn. of the O liberated by its decompn. in acid or alk. soln. is also studied. From the results obtained, M. formulates as a method for the estn. of the active O of Na_2O_2 , its decompn. in alk. soln., in the presence of $CuSO_4$, and the measurement of the gaseous O so liberated. The advantage of this method over that of Archlutt (*Analyst* **20**, 3-5(1895)) is that the decompn. is complete in two minutes, and that the evolved O is free from CO_2 . By means of these new methods of estn. M. shows that the action of the atm. on Na_2O_2 is principally due to the presence of moisture. J. C. S.

The electrometric titration of the halides in the presence of one another. H. H. WILLARD and F. FENWICK. *J. Am. Chem. Soc.* **45**, 623-33(1923).—The total halide content of a soln. can be detd. by electrometric titration with $AgNO_3$ soln. with the bimetallic electrode system. The break at the end-point is the poorest with the chloride but the slight rise in potential followed by a slow fall can be detected easily with a little practice. For the detn. of Br^- in the presence of Cl^- and I^- , the direct titration in HCN soln. to $BrCN$ by $KMnO_4$ is too slow to be followed when the bimetallic electrode is used but can be accomplished with the usual monometallic system if the titration curve is plotted. A slight empirical correction of -0.10 cc. for $0.1 N KMnO_4$ is necessary and often a sub-maximum occurs before the true end-point. Iodide if present is also oxidized to ICN but a selective detn. of the I^- is possible so that the Br^- can be detd. rapidly even in the presence of considerable Cl^- or I^- . Iodide may be titrated accurately electrometrically by means of this titration in all concns. of Cl^- and in moderate concns. of Br^- . A better method, however, is the oxidation of I^- to IO_3^- by an excess of $NaBrO$ and electrometric titration of the excess by arsenite. W. T. H.

Detection of fluorine. B. FETKENHEUER. *Wiss. Veröffentl. Siemens-Konzern* [3] 1, 177(1922).—The substance is heated with sand and a few cc. of H_2SO_4 at 90° in a test-tube. On shaking the tube, the presence of F is shown by the acid collecting into oily drops, which appear not to wet the surface of the glass. With 2 g. of substance, 0.01% of F may be detected after heating for one min. Insol. fluorides such as AlF_3 must first be fused with Na carbonate and sand; the fused mass is then heated as above with H_2SO_4 . J. C. S.

The volumetric estimation of small amounts of phosphorus using a standard solution of methylene blue. W. M. THORNTON, JR., AND H. L. ELDERICE, JR. *J. Am. Chem. Soc.* 45, 668-73(1923).—Quantities of P not exceeding about 0.5 mg., such as are obtained in the analysis of steels using 1-g. samples, can be detd. accurately by titration with methylene blue soln. The yellow $(\text{NH}_4)_2\text{PO}_4 \cdot 12\text{MoO}_4$ ppt. is dissolved in NH_3 soln. and the 6-valent Mo is reduced to the 3-valent condition by treatment with Zn and HCl out of contact with O_2 . The reduced Mo is oxidized back to the 6-valent condition by methylene blue which is decolorized thereby. When the soln. is blue, the end-point is reached. The method fails when considerable Mo is present because of the formation of blue reduction products of Mo. W. T. E.

The electrometric determination of sulfur in soluble sulfides. H. H. WILLARD AND F. FENWICK. *J. Am. Chem. Soc.* 45, 645-9(1923).—Sulfide may be titrated with 0.05 N AgNO_3 soln. contg. an excess of NH_3 . The electrometric end-point with the bimetallic electrode system is unusually sharp. The e. m. f. rises slowly at first and there is a rise of 200-400 millivolts just before the end-point is reached: at the completion of the reaction there is a very abrupt potential drop. The titration succeeds in the presence of SO_3^{--} , SO_4^{--} , $\text{S}_2\text{O}_3^{--}$ and S_2^{--} . W. T. H.

The successive titration of boric acid and phosphoric acid. I. M. KOLTHOFF. *Chem. Weekblad* 19, 449-50(1922).—The method is based on the fact that the acid properties of boric acid almost disappear after adding neutral Na citrate. The soln. contg. both acids is first neutralized to dimethyl yellow, after this, an excess of Na citrate is added and the soln. is titrated with 0.1 N NaOH until phenolphthalein is slightly rose, which means that phosphoric acid is present as secondary salt. Mannitol is then added and the soln. is titrated until phenolphthalein remains distinctly red which means that $p_H = 8.7$. The quantity of alkali, used in the last titration, corresponds to the boric acid present. R. BEUTNER

Iodometric studies. II. BOHDAN KÖHLER. *Chem. Listy* 16, 87-91(1922); cf. C. A. 15, 996.—The best results in the iodometric titration of tin are obtained by dissolving the tin in 6 N HCl, adding to this a known amt. of I dissolved in KCNS and detg. the excess of I with a standardized $\text{Na}_2\text{S}_2\text{O}_4$ soln. Contrary to the observation of Zulkowski and Bruhns (*J. prakt. Chem.* 103, 351(1859)), the velocity of the reaction $\text{Cr}_2\text{O}_7^{--} + 14\text{H}^+ + 6\text{I}^- \longrightarrow 2\text{Cr}^{+++} + 7\text{H}_2\text{O} + 3\text{I}_2$ is quite considerable. The titration of tin by means of $\text{K}_2\text{Cr}_2\text{O}_7$ soln. gives exact results if atm. O is excluded from the solus. Since it is, in practice, difficult to have air-free solns. of $\text{K}_2\text{Cr}_2\text{O}_7$, a correction of +0.068 mg. of tin per c. c. of aq. aerated $\text{K}_2\text{Cr}_2\text{O}_7$ soln. is advocated. This correction is based on the assumption that the soly. of O in decinormal $\text{K}_2\text{Cr}_2\text{O}_7$ soln. is little different to that in pure water. J. C. S.

The tinning test. K. YOKOBORI. *Researches Electrotech. Lab. Japan No.* 109, 43 pp.(1922).—As the dissolving power of Na sulfide soln. upon tin varies with the S content, it is necessary to define the compn. of the sulfide soln. used in Glover's tinning test. Y. prepd. about 70 kinds of sulfide soln. and examd. their solvent action upon tin. 22% solns. of Na_2S_3 and $\text{Na}_2\text{S}_{2.5}$ were found to be the strongest, while Glover's standard soln. corresponds to 19% soln. of Na_2S_4 and has only a weak dissolving power. Sulfide soln., prepd. by dissolving 10.7 g. of S into hot NaOH soln. contg. 100 g. NaOH

and dilg. to sp. gr. 1.142 after cooling, has nearly the same strength as Glover's standard soln. From these results, Y. proposes for testing tinned Cu wires (1) the use of the above-mentioned S-NaOH soln., which can be easily prep'd. in the same strength at any place and is preferable to Glover's standard soln. because of its stability and definiteness; and (2) the use of 22% soln. of $\text{Na}_2\text{S}_2\text{O}_3$ to save time compared with Glover's standard soln.

W. OGAWA

New method for estimating volatile substances in air. E. FRITZMAN AND K. MACJULEVICH. *J. Russ. Phys. Chem. Soc.* 52, 212-26(1920).—To est. the content of light petroleum vapor in air, the latter is first freed from dust, moisture, and CO_2 by passing it through tubes contg., in order, soda lime, CaCl_2 , P_2O_5 , and cotton wool, the light petroleum being retained in two U-tubes packed with Mg turnings and cooled in liquid air.

J. C. S.

Effect of iron on the iodine titration of arsenate. F. L. MELVILL. *J. S. African Chem. Inst.* 5, 3-5(1922).—The interference of ferric salts in the titration of arsenate soln. by I soln. may be prevented by the following procedure. The slightly acid arsenite soln., contg. not more than 0.1% of iron (expressed as Fe_2O_3), is treated with about one-half the quantity of I soln. required to oxidize all the arsenite, 10 cc. of satd. NaHCO_3 soln. are then added, and the titration is completed. In this way the whole of the iron is ppt'd. as ferric arsenate and no longer interferes with the titration. J. C. S.

The determination of lime by titration. A. VÜRTHEIM AND G. H. C. VAN BERS. *Chem. Weekblad* 19, 450-2(1922).—The well known method of dissolving and titrating the CaC_2O_4 ppt. is exam'd. and found to agree with the gravimetric method if in pptg. Ca the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ is added to the cold acid soln. and after that the soln. is boiled and made alk. to NH_3 .

R. BRÜTNER

Detection, elimination and determination of ammonia in hydroxylamine hydrochloride. R. GROS. *J. pharm. chim.* 26, 449(1922).—The presence of NH_4Cl , 81% in a "pure" com. sample of $\text{NH}_2\text{OH} \cdot \text{HCl}$ (A), prevented an exact detn. of HCHO by Brochet and Cambier's method (titrating the HCl liberated, using Me orange). To detect NH_4 , destroy the A in a nitrometer with a definite excess of I in presence of NaAcO or KHCO_3 , eliminate the excess of I with $\text{Na}_2\text{S}_2\text{O}_3$, then test for NH_3 as usual, or add NaBrO and measure the N set free. To clininate and det. the NH_3 , warm the aq. soln. of A in boiling H_2O with KHCO_3 , collect the NH_4HCO_3 in standard H_2SO_4 by suction and titrate back. When A is thus freed from NH_3 , it gives a sharp end reaction in the above test for HCHO .

S. WALDBOTT

The iodine content of common salt. P. FLEISSIG. *Schweiz. Apoth. Ztg.* 60, 591-6(1922).—The Swiss saline waters and their salts of Bex, Rheinfelden (R) and Wildegg were exam'd. for their I content. The method of Winkler (oxidation of KI with $\text{Cl-H}_2\text{O}$ to KIO_3 , addn. of KI and H_3PO_4 and detn. of the I set free (cf. C. A. 9, 1517; 10, 867, 2674, 2777) cannot be used, as these salts contain some oxidizing substance. Conc'n. of the I content in the salts by repeated pptn. of their aq. solns. with EtOH is necessary before any I can be detd. Fresenius' method being sensitive to 0.001 g. I per l., fails to show I in the R soln., which thus contains less than 0.001 g. per l. J. Kunz's method (setting free I with H_2O_2 in H_2SO_4 soln.) gave the same result. The Bex saline H_2O showed about 0.002 mg. I per l. Electrometric detns. by v. Neergaard, sensitive to $10^{-4}N$ I, indicated no I in the salts of Bex and R, but showed 2.3 mg. for the Bex, and 0.5-0.7 mg. for the R soln. The Wildegg H_2O contains 4.4 g. salts and 0.008 g. NaI per l.

S. WALDBOTT

The determination of potassium in potassium salts rich in sulfates. A. VÜRTHEIM. *Verslag. Land. Onderzoek. Rijkslandbouwprefsta.* 24, 249-58(1920).—In the pptn. of sulfate by BaCl_2 , the BaSO_4 formed contains K_2SO_4 , which causes a loss of K in the analysis. This is also the case in acid soln. To prevent this loss of K, the largest part

of the sulfate should be pptd. by CaCl_2 as CaSO_4 . Also, the presence of Ca^{++} in the soln. prevents the K^+ from being pptd. with BaSO_4 . R. BEUTNER

The bitartrate titration method for the determination of potassium. W. A. ALBERTI-RAKHORST. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* **26**, 89-95(1922).—The old method of pptg. K by adding tartaric acid and Na tartrate and titrating the ppt. with 0.1 N NaOH (cf. *Z. anal. Chem.* **1**, 59(1862); **4**, 215(1865); **6**, 257(1867); **8**, 505(1869); **11**, 474(1872); *Chem.-Ztg.* **38**, 585 and 615(1914)) was tested and found unsatisfactory; the values for K are always too small and vary in an irregular manner.

R. BEUTNER

The determination of potassium as alum. MILE DE LE PAULLE. *Compt. rend.* **176**, 105-7(1923).—Small quantities of K can be estd. approx. by taking advantage of the fact that potash alum is practically insol. in 30% alc. Thus, after the Berzelius method of decomposing about 2 g. of silicate with HIF and H_2SO_4 it is recommended to expel all excess of acid and dissolve the residual sulfates in a little hot water. Then add alc. and water so that 35 cc. of water are present and 15 cc. of alc. The rock is likely to contain more than sufficient Al to form the desired alum. The alum will crystallize out if kept at 0° for 24 hrs. The crystals should be washed with 50% alc. and air-dried before weighing. Under favorable conditions the results may be within 10% of the truth. W. T. H.

Determination of reducing sugars by means of Fehling solution with methylene blue as internal indicator. J. H. LANE AND L. EYNON. *J. Soc. Chem. Ind.* **42**, 32-7T(1923).—Methylene blue is decolorized by boiling hot solns. of aldoses and ketoses but if Fehling soln. is also present the decolorization does not take place until enough sugar soln. has been added to reduce all of the bivalent Cu. Moreover, upon adding a little more Fehling soln. the blue color returns. In the detn. of reducing sugars with methylene blue, a 1% indicator soln. is recommended. First det. the approx. reducing power of the sugar soln. and then, in the analysis proper, add within 1 cc. of the amt. necessary to reduce 10-25 cc. of Fehling soln. Heat to boiling in a flask, add 3-5 drops of the indicator soln. and titrate with more sugar soln. until the blue color disappears. It is only necessary to boil the reaction soln. 3 mins. in all. Tables are given for invert sugar, dextrose, levulose, maltose and lactose showing the various factors to use in calcg. the reducing sugar content from the vol. required to reduce a given vol. of Fehling soln. W. T. H.

Volumetric determination of copper, and application to the determination of reducing sugars. ED. LASAUSSE. *J. pharm. chim.* **26**, 401(1922).—In the detn. of reducing sugars, L. combines the method of Quisumbing and Thomas (*C. A.* **16**, 37) with his own procedure for detg. the resulting Cu_2O . Dissolve the Cu_2O in very little HNO_3 and oxidize HNO_2 formed, by KMnO_4 (cf. *C. A.* **14**, 33), filter, add cryst. NaAcO , then KI and titrate with $\text{Na}_2\text{S}_2\text{O}_3$ soln. The method, given in detail, is accurate to 1% of theoretical amts. S. WALDBOTT

The separation of iron and aluminium from manganese and certain other elements. G. E. F. LUNDELL AND H. B. KNOWLES. *J. Am. Chem. Soc.* **45**, 676-81(1923).—It has been thought that the basic acetate or BaCO_3 methods were more satisfactory for the sepn. of Fe^{+++} and Al^{+++} from Mn^{++} than pptn. of Fe^{+++} and Al^{+++} by means of NH_4OH in the presence of NH_4Cl . It is shown, however, that if the Fe and Al are pptd. cautiously by adding dil. NH_4OH dropwise to a hot soln. contg. 5 g. of NH_4Cl in 200 cc. until methyl red indicator turns to a distinct yellow, the ppt. contains very little Mn and by a second pptn. in the same way a better sepn. is accomplished than by means of the much more tedious basic acetate method. P and V interfere but slightly if the Fe and Al preponderate, as is usually the case, but it is then necessary to add Fe^{+++} when the basic acetate or BaCO_3 sepn. is used. Under the above conditions,

which are those recommended by Blum for the pptn. of Al, the sepn. of Fe^{+++} and Al^{+++} from Co^{++} , Cu^{++} and Zn^{++} is incomplete but a large excess of NH_4Cl improves it. For Cu and Zn a better sepn. is accomplished when an excess of NH_4OH is used but this causes incomplete pptn. of Al.

W. T. H.

The electrometric determination of iron and vanadium when present together. E. MÜLLER AND H. JUST. *Z. anorg. allgem. Chem.* **125**, 155-66(1922).— Fe^{++} solns. are more vigorous reducers than are vanadyl solns. If KMnO_4 is added slowly to a mixt. of these substances the first sudden change in e. m. f. corresponds to the complete oxidation of Fe and the next sudden change, preferably with the temp. now raised to 70° ; shows the oxidation of V.

W. T. H.

The microchemical detection of arsenic. A. PIUTTI AND E. BOGGIO-LEGA. *Gazz. chim. ital.* **52**, II, 48-55(1922).—It was desired to know if the reactions for H_2AsO_4 with AgNO_3 with the Mg reagent and with NH_4 molybdate can be used in place of the usual Marsh test for As. Accurate data on these reagents as micro-reactions are not available. The results showed that the molybdate reagent is most sensitive for detecting As as H_2AsO_4 . It can be detected in a single drop of a soln. contg. 0.001 mg. As per cc. or $1/10,000$ mg. The test cannot be made directly on the liquids obtained from material from cadavers. In this case it is first sepd. as As_2S_3 and oxidized with HNO_3 . Test expts. showed that H_2AsO_4 in the presence of H_2SO_4 ppts. As_2S_3 with H_2S in 24 hrs. when 0.005 mg. or more As per cc. is present. The test is a valuable exploratory test since the limit of sensitivity of the Marsh test is 0.01 mg. As unless unusual precautions are taken. The NH_4 molybdate soln. was prepd. thus: 1 cc. 3% NH_4 molybdate soln. + 10 cc. 3.4% NH_4NO_3 + 39 cc. 40% HNO_3 . A glass ("portaoggetti") was warmed and a drop of the As soln. (0.020-0.004 mg. As per cc.) placed upon it. It was evapd. $2/3$ in a small flame, a drop of the Mo reagent was added and the mixt. again evapd. but not too slowly. Photomicrographs are given to show the normal and abnormal ppts. This evapn. requires 6-7 mins. A drop of a soln. contg. 5 g. NH_4NO_3 , 4 cc. HNO_3 and 100 cc. H_2O was added to the residue. Characteristic yellow crystals of the arsenomolybdate sep. which are easily distinguished from the colorless acid molybdate crystals. Practice is required. Some additional details are given.

E. J. WITZEMANN

Rapid analysis of aluminium alloys. G. W. WALKER. *Chem. Met. Eng.* **28**, 242 (1923).—Directions are given for applying the well known persulfate method for Mn and the electrolytic method for Cu to the analysis of Al alloys.

W. T. H.

Sampling spotty gold ores. ERNEST A. HERSAM. *Eng. Mining J.-Press* **115**, 217-8(1923).—In discussing the paper by Demond and Halferdahl (*C. A.* **17**, 506) it is claimed that the data there apply to only a special case and that the conclusions drawn are contrary to current practice, without regard to the previous work by D. W. Brunton (*Trans. Am. Inst. Mining Eng.* **25**, 826(1895)).

S. E. CARLSON

The colorimetric estimation of pyrogallol, gallotannin and gallic acid. C. A. MURCHELL. *Analyst* **48**, 2-15(1923).—Methods for the detn. of tannin by the hide powder method are not altogether satisfactory to the ink-maker. The proposed method is based upon the violet color produced when FeSO_4 reacts with gallotannin in the presence of tartaric acid. As reagent a soln. contg. 0.1 g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.5 g. of Rochelle salt has been found suitable. It must be prepd. freshly. Either pure pyrogallol or pure gallic acid may be used as a standard of comparison but the latter is preferable. As standard soln. one contg. 0.1 g. of pure substance in 100 cc. of water is recommended. Use 1 cc. of this soln. to about 95 cc. of water in the calorimetric comparison. Add 2 cc. of the above reagent to the standard and to the soln. of tannin, make up to the 100-cc. mark and compare the colors both vertically and horizontally. If the colors are both dark, take 50 cc. of each and compare again. Run out the darker

soln. until its color matches the weaker when viewed vertically. Dil. each to 100 cc. and again compare at different levels. The coloration is so stable that the process of diln. and comparison may be repeated several times without recharging the tubes. If the unknown soln. contains very little tannin it is advisable to repeat with a smaller amt. of standard. The results obtained in the analysis of various materials contg. tannin indicate that the av. tannin is a mixt. of glucosides but is chiefly a digallyl glucoside with a digallic anhydride of the type described by Nierenstein (*C. A.* 15, 1694). The colorimetric ratio varies with different tannins because the gallotannin content varies. The tannin from sumac, for example, does not appear to contain any of this substance so that the colorimetric method fails. Mixts. of *gallotannic acid* and *gallic acid*, *commercial tannic acids*, *nut galls*, *roasted galls*, *oak apple galls*, *Chinese galls*, *myrobalans*, *valonia*, *divi-divi*, *sumac* and *tea* were tested by the method and data obtained on the fermentation of gallotannin showing that such fermentation often caused complete destruction of the gallic acid formed by hydrolysis.

W. T. H.

A new method for the detection of methanol. REINO HAMÄLÄINEN. *Acta Soc. Med. fennic. "Duodecim."* 3, 1-6(1921).— CH_3O from the oxidation of MeOH by KMnO_4 in $\text{EtOH-H}_2\text{SO}_4$ soln. is detected by addn. of methyl violet- H_2SO_4 decolorized by oxalic acid; a dark- to light-blue coloration is formed.

J. C. S.

The methods of determining formaldehyde by oxidation. R. GROS. *J. pharm. chim.* 26, 415-25(1922).—The known methods for detg. HCHO , notably that of the Codex, fail to give exact results since oxidation extends to CH_2O_2 formed. The Romijn method, while simple, cannot be used when acetone is present. The *Nessler reagent method (A)* (*C. A.* 16, 3281) is not affected by CH_3O_2 nor acetone; it gave const. results on a 35.5% soln. The definite *bisulfite compd.* $\text{NaHSO}_3 \cdot \text{CH}_3\text{O} \cdot \text{H}_2\text{O}$ may be used in checking this method. It reacts with a total of I_2 in 2 steps: In the 1st, NaHSO_3 is instantly oxidized by I_2 ; titrate back with As_2O_3 soln. in presence of a known amt. of KHCO_3 ; then proceed by method A. If in the 1st step, the action of I_2 is prolonged, the CH_2O is very slowly oxidized (cf. Bougault, *C. A.* 11, 2756); but the total amt. of I consumed is the same, *i. e.*, I_2 .

S. WALDBOTT

Technical sedimentation analysis (HAHN, HAHN) 18. Solubility of Berlin blue (KOHn) 2.

BOUTOR: Étude du dosage de sucres réducteurs au moyen des liqueurs cuproalcalines. Paris: E. Le Francois. Fr. 8.

CARNOT, ANOLPHE: Traité d'analyse des substances minérales. Vol. IV. Métaux (2nd Pt.). Paris: Dunod. 1050 pp. Fr. 65, bound Fr. 69.50.

FERNÁNDEZ-LADRERA, J. M.: Métodos recomendados en el análisis químico cuantitativo de hierros y aceros. Madrid: Romo. 99 pp.

JESSOP, C. M.: Elementary Analysis. New York: McMillan & Co. \$2.25.

MILLER, EDMUND H.: Calculations of Analytical Chemistry. 3rd Ed. revised and enlarged. London: McMillan. 201 pp. 9s.

SCHMIDT, ERNST: Anleitung zur qualitativen Analyse. 9th revised Ed. Berlin: Julius Springer. 114 pp. M 45.

Low, A. H.: Technical Methods of Ore Analysis. 9th Ed. Revised. New York: John Wiley & Sons, Inc. 348 pp. \$3.50. Reviewed in *Ind. Eng. Chem.* 15, 324(1923).

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

Keeleyite, a new lead sulfantimonite from Bolivia. S. G. GORDON. *Proc. Acad. Natural Sci. Phila.* 74, 101-3(1922).—This occurs as radiating aggregates of acicular (perhaps orthorhombic) crystals with pyrite and quartz in the San José mine at Oruro. It is dark gray with bright metallic luster and gives a grayish black streak; $d = 5.21$, $H. = 2$. Analysis by Whitfield gave: Pb 25.80, Sb 43.46, Cu 2.25, Fe 2.77, S 24.54, quartz 1.18, total 100. Deducting 8.15% of admixed sulfides, this gives the formula $2PbS.3Sb_2S_3$, corresponding with rezbanyite ($2PbS.3Bi_2S_3$). The comps. of the known lead sulfantimonites are represented on a triangular diagram. J. C. S.

Minerals from Ljubija, Bosnia. RUDOLF KOECHLIN. *Min. petr. Mitt.* 35, 1-12 (1921).—The iron ore at Ljubija, near Prijedor, consists of cryst.-granular chalybite with impregnations of galena, pyrite, and chalcopyrite. Near the surface, the chalybite is altered to limonite, with which are various other secondary minerals. These, including the rarer species leadhillite, pyrochroite, and beudantite, are described.

J. C. S.

Jades of Middle America. H. S. WASHINGTON. *Proc. Nat. Acad. Sci.* 8, 319-26(1922).—This paper presents the results of a study of jade beads, disks, etc., found at Chichen Itza, Yucatan; ancient Mexican beads; and objects from Copan, Honduras. The phys., mineralogical and chem. characters of these and other Am. jades exhibit great variety. Dominant colors are green and gray. Textures range from decidedly coarse to very fine-grained. Hardness 6.5 to 6.75. Sp. gr. ranges from 3.335, about that of jadeite, to 2.667, about that of oligoclase. Chem. analyses of 12 samples are given, also their lithologic compn. in terms of the 4 mols.: jadeite, diopside (sometimes including very small amts. of hypersthene or wollastonite and a little Fe_2O_3), albite (including minute amts. of orthoclase), and anorthite. In 6 jadeites, as detd. by Merwin, the range of α was 1.650 to 1.666, that of γ 1.667 to 1.693. These jades differ from the usual Burma and Chinese jades in the constant presence of considerable amts. of diopside with the jadeite in the pyroxene, and in the presence of albite in most of the series. The material of the Middle Am. jade objects is of Am. and not Asian provenance. The series extends from pure *tuxtilite* (diopside-jadeite 1 : 1) to nearly pure albite. The name *mayaite* is proposed for this series. L. W. RIGGS

Note on the mineralogical composition of some specimens of Teotihuacan "jade." CARLOS F. DE LANDERO. *Mem. rev. soc. cient. Antonio Alzate* 40, 519(1922). O. B. H.

Lead ores, containing silver, in the province of Mendoza, Argentina. Z. S. BEIJL. *De Ingenieur* 37, 831-44, 869-78(1922).—B. gives a detailed description of the geological conditions and the mining of the ores. Their Ag content varies from 100 up to 1800 g. per ton, in one case 8400 g. The occurrence of bitumen is also described.

R. BEUTNER

Copper deposits of the Tyrone district, New Mexico. SIDNEY PAIGE. U. S. Geol. Survey, *Professional Paper* 122, 51 pp.(1922).—A geological description of the district is given. The principal Cu deposits are chalcocite ore bodies in porphyry and granite. They owe their value to the enrichment of pyrite and chalcopyrite by descending rain water. No primary ore is mined in the district. The phys. and chem. conditions under which primary mineralization, alteration and enrichment occurred are described by many chem. equations and diagrams. Ore bodies of several mines are shown by maps of the shafts, drives and cross-cuts. The min. of Cu in the rock to constitute ore is detd. by a balance between the total costs of mining and the price of Cu; much of the rock contains from 1.75 to 2.5% of Cu. L. W. RIGGS

Geology of the York tin deposits, Alaska. E. STEINTMANN AND S. H. CATHCART.

U. S. Geol. Survey, *Bull.* 733, 25 pp.(1922).—The York tin region is the most westerly portion of the N. Am. continent. The geology of the region and of 6 near-by areas is given, and 52 locally occurring minerals are described, with simple tests to aid the prospector in their identification. Like other Sn deposits of the world the York occurrences are in granite or rocks closely associated with granite such as intruded limestone. Several mines and prospects are described but more work is necessary before reliable estimates of the probable yield of Sn from this region can be given. L. W. RIGGS

Geology of the Range oil field, Texas. FRANK REEVES. U. S. Geol. Survey, *Bull.* 736-E, 111-70(1922). L. W. RIGGS

Potash in the greensands of New Jersey. G. R. MANSFIELD. U. S. Geol. Survey, *Bull.* 727, 142 pp.(1922).—The greensand marl belt extends across the state in a south-westerly direction for about 100 miles. The K in the sands exists chiefly in the mineral glauconite $KFe^{+++}Si_2O_5 \cdot H_2O$. Five type areas were explored by borings. A conservative est. places the K_2O that could be mined by open-pit methods at 256,953,000 tons, or enough to supply the U. S. on the basis of 1910-1914 consumption for 1000 years. Should it become practicable to use underground methods of mining, the available quantity of K would be enormously increased. Success in producing K from greensand depends on ability to compete with importations from Germany and with American producers of K from other sources. Many mechanical analyses and about 300 quant. tests for K_2O are reported, a large majority of the samples showing K_2O above 6%. Three closely agreeing samples analyzed by R. K. Bailey averaged SiO_2 50.93, Fe_2O_3 17.63, FeO 3.09, Al_2O_3 5.23, CaO 1.34, MgO 3.74, K_2O 7.03, Na_2O 0.83, CO_2 0.46, P_2O_5 0.81, H_2O 9.21%. L. W. RIGGS

Mineral resources of Illinois in 1917 and 1918. N. O. BARRETT. Illinois State Geol. Survey, *Bull.* 38, 25-112(1922).—The history of the development of the mineral resources of Illinois, the location, production, value and future outlook for the yield of various economic minerals are given with much detail. Geology and mineral resources of the Edgington and Milan quadrangles. T. E. SAVAGE AND J. A. UDDEN. *Ibid.* 117-208.—Over 70 pp. are devoted to an elaborate description of the geological features. The principal mineral resources comprise coal, shale and clay, limestone, sand and gravel, and water; to these may be added the soil, which is the chief source of wealth in the area. Chem. analyses of 13 samples of coal, 6 samples of water from St. Peter sandstone, and sanitary analyses of 22 samples of Miss. River water are tabulated. Geology and mineral resources of the Avon and Canton quadrangles. T. E. SAVAGE. *Ibid.* 209-71.—This area includes about 450 sq. mi., and in it 4 different coal beds are worked. Analyses of 53 samples of the coal are tabulated. Clay and shale occur in apparently unlimited amts. L. W. RIGGS

Geology and mineral resources of the Morris quadrangle. H. E. CULVER. Illinois State Geol. Survey, Ext. from *Bull.* 43, 114 pp.(1922).—The topography, descriptive, structural and historical geology are given in 94 pages. Coal, shale and clay, stone, sand and gravel, water and soils comprise the known resources. Eleven samples of coal from "No. 2" averaged about 11,000 B. t. u. on the "as received" basis. Shale and clay suitable for fire-clay, brick and tile occur in this area, also sandstone and limestone fit for structural work. Water is abundant, mostly hard, some sulfurous. Soils are fertile except where the bed rock lies near the surface. L. W. RIGGS

Peridotite dikes in Scott County, Arkansas. H. D. MISER AND C. S. ROSS. U. S. Geol. Survey, *Bull.* 735-H, 271-8(1922).—A lithologic description of the peridotite is given. That of Scott Co. is similar to the diamond-bearing peridotite of Pike Co., but should diamonds be found in it, they could not be recovered economically on account of the narrowness of the dikes and the hardness below a few feet of weathered surface. L. W. RIGGS

Annual report of the director of the U. S. Geological Survey. G. O. SMITH. 43, 79 pp. (1922).

L. W. RIGGS

Rock strata gases in mines of a Nevada mining district E. D. GARNER. *Bur. Mines, Repts. of Investigations* 1922, No. 2427, 4 pp.—Irrespirable gases, generally N_2 or CO_2 , appear to "ooze" from cut surfaces, crevices and fissures either slowly or rapidly and accumulate so as to endanger life in unventilated spaces or abandoned raises. Analysis of 13 samples taken from levels 600 to 1100 ft. deep gave a relative humidity of 60 to 97, CO_2 0.04 to 1.26%, O_2 1.62 to 20.91, and N_2 79.05 to 98.05. Two theories are advanced to account for the presence of N_2 above that in ordinary air. I. W. R.

Occurrences of fire damp on the Far East Rand. T. N. DEWAR. *J. Chem. Met. Soc. S. Africa* 22, 34-5 (1921); cf. *C. A.* 17, 1204.—Discussion. C. J. Gray reports several occurrences of fire damp on the Rand. Fire damp seems to originate in the shales in the Witwatersrand series rather than in coal seams in overlying strata. J. Watson calls attention to the fire damp encountered in limestone associated with rock salt.

LOUIS JORDAN

* DEWEY, HENRY: *Memoirs of the Geological Survey. Special Reports in the Mineral Resources of Great Britain. Vol. 21. Lead, Silver-lead, and Zinc Ores of Cornwall, Devon and Somerset.* Southampton: Ordnance Survey Office. London: E. Stanford, Ltd. 72 pp. 2s. 6d. Reviewed in *Nature* 109, 6 (1922).

SCHETTLER, RUDOLF and EPPLER, ALFRED. *Lehrbuch der Chemie mit Einführung in die Mineralogie und Geologie für Realschulen, Lyzeen, höhere Mädchenschulen und verwandte Anstalten.* Leipzig: Quelle & Meyer. 309 pp.

SMITH, BERNARD: *Memoirs of the Geological Survey. Special Reports on the Mineral Resources of Great Britain. Vol. 19. Lead and Zinc Ores in the Carboniferous Rocks of North Wales.* Southampton: Ordnance Survey Office. London: E. Stanford, Ltd. 162 pp. 5s. 6d. Reviewed in *Nature* 109, 6 (1922).

WOLFF, FERDINAND VON: *Einführung in die allgemeine Mineralogie, Kristallographie, Kristallphysik, Mineralchemie.* Leipzig: Quelle and Meyer. 135 pp.

9—METALLURGY AND METALLOGRAPHY

N. J. DEMOREST, R. S. WILLIAMS

Note on an apparatus for small scale flotation tests. H. I. SULMAN and H. F. K. PICARD. *Bull. Inst. Mining Met.* 1923, No. 220, 1-10.—Ten to 12 g. of ore may be treated in the apparatus described. Reliable indications are afforded as to the nature of the results obtained by flotation and with as great accuracy as tests on larger scale equipment. The app. and manipulation are described in detail. C. H. HERTY, JR.

Slime flotation plant at the Broken Hill South Mine. W. E. WAINWRIGHT and T. A. READ. *Chem. Eng. Min. Rev.* 14, 351-6 (1922):—The slime of this plant carries 10.7% Pb, 14.2% Zn and 5.9 oz. Ag per ton. The former flotation process gave a concentrate of 26.2% Pb, 34.8% Zn and 19.0 oz. Ag. This concentrate was so high in Zn that it was practically worthless. By use of small amts. of oil and violent agitation lab. expts. gave, with 0.5 lb. eucalyptus oil per ton and at a temp. of 20-4°, a Pb concentrate contg. Pb 71.0%, Zn 7.5% and Ag 46 oz., representing a recovery of 86.2% of the Pb and 84.5% of the Ag. With the same amt. of oil plus 100 lb. H_2SO_4 per ton a Zn concentrate contg. Zn 50.7%, Pb 4.5% and Ag 3.5 oz. per ton was made. The mill proper only recovers a Pb concentrate, however, by using a specially designed machine which is described in detail; some flow sheets also are given. The final product now because of a 60% Pb requirement of the smelter is Pb 61.6%, and 49.2 oz. Ag, representing a recovery of 79.7% on Pb and 84.4% on Ag.

W. A. MUELLER

Proposed method for reducing mineral waste in the Wisconsin zinc district, Wisconsin. W. H. COGHILL AND C. O. ANDERSON. *Bur. of Mines, Tech. Paper* 301, 66 pp. (1922).—This paper deals with the metal losses in mining and treatment of the Pb and Zn ores of the Mississippi Valley. The concentrate grade is as low as 25%, owing to pyrite being present and only jigging practice in the region. The tabling of the tailings was done in lab. quantities and a concentrate of from 20 to 25% Zn made. In trying flotation on the tailings and ore, expts. using CuSO_4 and other chemicals were attempted with more or less success. The nature of the water, ores and oils used are discussed briefly, together with a resumé of the process attempted and the results obtained.

W. A. MUELLER

Utilization of metallurgical slag. ERNESTO BLANCHI. *Giorn. chim. ind. applicata* 4, 462-3(1921); cf. *C. A.* 16, 3053.—A few further notes on the previous articles. B. proposes to recover the Mn used for desulfurizing, by reduction processes, utilizing the residual heat in the slags after pouring.

ROBERT S. POSMONTIER

The operation of blast furnaces with green wood. M. A. PAVLOV. *Messageur technico-économique russe* 2, 292-6(1922); *Rev. métal.* 20 (Extraits), 84-5(1923).—Prudhomme (*C. A.* 15, 653) made certain errors in calcg. the heat balance of the blast furnace at Corrale, Chile. The process is economical only for a blast furnace erected in a virgin forest or where wood can be floated to the plant. As compared to operation with charcoal, it eliminates the installation of the carbonizing plant and gas purification plant; but the production of Fe per m^3 of blast furnace is reduced by 50% and over.

A. P.-C.

Calculating heat losses in furnaces. O. I. HANSEN. *Blast Furnace & Steel Plant* 10, 437-40(1922); 11, 117-22(1923).—The heat losses in boilers due to incomplete combustion of the fuel cannot be detd. with exactness with the ordinary Orsat app. H.'s method is to absorb the CO_2 in KOH and burn any H_2 , CH_4 and CO present by heating the gas in a Pt capillary tube and observing the contraction. From this the percentages of combustible gases and the heat loss may be calcd. by suitable formulas. The analysis is carried out over H_2g , and errors due to temp. change in the measuring buret are cut down by air cooling the water-jacketed buret and by using a compensating U-tube pressure equalizer. The method is claimed to be much superior to the ordinary Orsat method or to slow combustion or explosion methods. C. H. H., Jr.

Raw materials and their preparation for blast furnace operations in North America. H. A. BRASSERT. *Stahl u. Eisen* 43, 1-9, 44-9, 69-73(1923).

W. A. MUDGE

Investigation of losses in copper blast-furnace slag. D. F. STEDMAN. *Eng. Mining J. Press* 114, 1023-7, 1072-6(1922).—Blast-furnace slags produced at the Trail, B. C., plant of the Consolidated Mining & Smelting Co. or slags produced under similar conditions formed the basis of this study. For the detn. of Cu the slag is best decompd. with SO_2 , HF and pyrogallol acid. The Cu in the converter slag was shown to be largely mat prills with considerable Cu silicate and some Cu sulfide dissolved in the slag, the Cu prills being held in permanent suspension by magnetite crystals. Equil. data were obtained by exptl. fusions in an elec. furnace and a const. loss of Cu found as the dissolved sulfide varies with the grade of mat. The probable losses with high-grade mat were calcd.

L. T. FAIRHALL

Developments in the open hearth. M. F. MILLER, JR. *Blast Furnace & Steel Plant* 11, 48-51(1923).

E. J. C.

Improvements in open-hearth furnaces. E. C. COOK. *Blast Furnace & Steel Plant* 11, 61-4(1923).—Description of the Loftus variable-pressure method of firing open-hearth furnaces and of the Naismith mech. neutral joint.

E. J. C.

Fuel gas question in the steel industry. F. J. DENK. *Iron Age* 111, 401-5, 451(1922).—The types discussed are natural gas, Duo (a combination of water and

coal gas), coke oven gas, and producer gas. Analyses of the gases and the calcs. of the vols. of the products of combustion in each case are given. The nature of the losses of heat are shown and the reasons for same simply illustrated. The use of waste gases is considered and in the final conclusion it is shown that the B. t. u. value of a gas is not the detg. factor as to its value to the process for which it is used. W. A. M.

Metallurgy of mercury. II. ALDO ANTONAZ. *Giorn. chim. ind. applicata* 4, 525-8(1922); cf. C. A. 16, 1725.—Treats of the substitution in Idria of the Spirek furnace for the older reverberatory furnace, with the advantages accruing. R. S. P.

Review of iron and steel literature for 1922. E. H. McCLELLAND. *Blast Furnace & Steel Plant* 11, 7-11(1923).—A bibliography with comments on the entries. E. J. C.

Developments in metallurgy of iron and steel. S. L. GOODALE AND K. D. DODD. *Blast Furnace & Steel Plant* 11, 4-6(1923).—A review. E. J. C.

The importance of physical chemistry in the metallurgy of iron. R. SCHENCK. *Stahl u. Eisen* 43, 65-9, 153-9(1923).—The importance of the phase rule and its applications in blast furnace practice are discussed. Curves and calcs. are given as illustrations. W. A. MUDGE

The manufacture of iron by means of raw coal in Siberia. M. A. PAVLOFF. *Messenger technico-économique russe* No. 2, (Feb. 1922); *Rev. métal.* 20 (Extraits), 33-4 (1923).—A discussion of the possibilities of using Vlassov coal (H_2O 1.55, 2.20; volatile 25.75, 23.30; fixed C 66.65, 70.90; ash 6.05, 3.60; S 0.74, 0.69%) directly in blast furnaces; these would probably have to be 18-24 m. high. This coal would give better results than other coals so used at present. A. PAPINEAU-COUTURE

Progress in the manufacture of Martin steel. A. BARBEROT. *Rev. métal.* 20, 1-26, 95-111(1923).—A detailed review of the development of the process, and of the equipment used, from the beginning until the present day. A. P.-C.

Application of colloid chemistry to production of clean steel. H. W. GILBERT. *Trans. Am. Inst. Mining Met. Eng.* No. 1221-S, 7 pp.(1923).—Dirty steel is unreliable, especially in resisting fatigue. Dirt is present in the molten metal as an emulsion or suspension of colloidal nature. Present methods tend to destroy such colloidal suspension, but they produce only relatively clean steel. Other methods of destroying such suspensions are known to the colloid chemist, but too little is known of the fundamental properties of colloids in molten metals to allow direct application of the other methods. Such fundamental knowledge should be sought and the making of both steel and non-ferrous alloys should be studied from the colloid viewpoint. JEROME ALEXANDER

Iron from pyrrhotite. F. H. MASON. *Can. Mining J.* 43, 708(1922).—Sufficient removal of Cu has been the bar to com. success in the past, but with improved methods of concn. this difficulty may be overcome. In the lab. at Trail, B. C., pure Fe has been made by an electrolytic method from pyrrhotite tailing from the dressing of the Sullivan mine ore. A. BUTTS

Use of peat coke for the fusion of cast iron in the cupola. Y. P. ZALESSEKY. *Messenger scientifique et technique russe* No. 6, 58-66(1922); *Rev. métal.* 20 (Extraits), 49-50 (1923).—The coke used contained H_2O 10, ash 5, C 74.4, H 2.32, O 7.8, N 0.5%; calorific value 6,600 cal., volatile matter 23%, wt. per m.³ 300 kg. Compn. of the org. matter was C 87.5, H 2.7, O and N 9.8%. Its properties were intermediate between those of coal, coke, and wood charcoal. The coke was sepd. into 3 grades: coarse (av. size 80-100 mm.) 30%, fine (av. size 25-30 mm.) 35%, dust 35%. The latter could be used only under the boilers and for the dryers. A blast of 225 mm. of water was used for the first test, and of 275 for the last two. Satisfactory results were obtained in the 3rd test with pig Fe 2,460 kg., scraps 1,230, small lumps ("masselottes") 1,230 (total 4,920), Donietz coke 164, anthracite 246, peat coke 820 (total 1,230 = 25% of metal), flux 213. With cupolas having straight sides and no upper tuyères the max. charge should not exceed

0.055 kg. per cm.² cross section; when the sides are curved it may be raised to 0.06–0.08 kg. The upper tuyères are harmful when peat coke is used. Owing to its low crushing strength (2–20 kg. per cm.²), the height of the charge should not exceed 4.25 m. It is useless to increase the section of the tuyères above 16% of the section of the cupola. An increase of 20% in the blast pressure increases the amt. of air about 14%; but the pressure should not exceed 400 mm. of water, as the peat coke would then be blown out. The heat balance is given, and also a formula for calcg. the amt. of air used.

A. PAPINEAU-COUTURE

Forced heating of Cowpers by the Pfoser-Siracke-Stumm process. P. LÉMOINE. *Rev. métal.* 20, 88–94(1923).—A discussion of the merits of this patented process (1913), whereby greatly increased speed of the combustion gases is obtained without any appreciable increase in the temp. of the flue gases.

A. P. C.

Copper. ANON. Bur. Standards, *Circ.* No. 73, 108 pp.(1922).—A summary of the chem., physical, and mechanical properties of Cu. Data are given for sources, refining, production, metallurgy, metallography, electrodeposition, working, heat treatment, discuses, and the effect of impurities. A complete bibliography is appended.

W. A. MUDGE

Properties and uses of titanium. R. J. ANDERSON. *Chem. Age* (N. Y.) 31, 27–30(1923); cf. *C. A.* 17, 526, 714.

E. J. C.

Consideration of some of the properties of metals. F. T. MURLLESS. *Dental Cosmos* 65, 145–55(1923).—A discussion of the physical properties of the precious metals, solders and soldering, alloys, the eutectic, liquidation, crystal., and annealing.

JOSEPH S. HEPBURN

The phenomena of diffusion in metals in the solid state and cementation of metals other than iron. III. Influence of the vapor tension of migratory elements in the formation of the cemented superficial layer. G. SIROVICH AND A. CARTOCETI. *Gazz. chim. ital.* 52, II, 233–45(1922).—In a previous paper on the cementation of Cu with Cr-Mn (*C. A.* 16, 3856) there were observed: (1) the formation at the surfaces of the bar of a layer of alloy with a definite concn. of the migratory element and (2) the transportation of this element into the interior of the bar. In this paper (1) will be discussed more fully. The simplest way to imagine the formation of this 1st layer is to admit that at the temp. of the expts. the cement shows a certain vapor or dissociation tension for the various elements that compose it so that the environment of the material being cemented is satd. with the vapors of the elements in question. Such a process would be a case of true sublimation and is discussed mathematically. If the vapor or dissociation tension of the alloy being produced is less than that of the element itself present in the cement this will prove that cementation occurs either through direct sublimation or by means of the decompn. and formation of special gaseous compds. of the element itself (cf. Giolitti, *C. A.* 6, 1124). There is a method of comparing the vapor tension that an element manifests in various alloys at different temps. even when the alloys are considerably below their m. ps. The method used was previously described (*C. A.* 16, 1063) and consisted in prolonging the cementation until the cementing element reached a constant concn. in the bar. For this purpose the cementation of Cu with Fe-Mn was repeated with alloys of the cement contg. I 19.5% Mn, 3.95% C; II 33.6% Mn, 4.48% C; III 56.6% Mn, 5.2% C; IV 76.8% Mn, 6.58% C, resp. The cement and Cu bars were prepd. as usual and the 4 expts. all placed in one Haraeus furnace at the same time and kept at 900° for 48 hrs. After allowing 48 hrs. for cooling 10 layers 0.1 mm. thick were shaved off each bar in the lathe and each layer was analyzed separately. The Mn contents of the layers in the 4 bars are shown in a graph. The result confirmed the interpretation in all but IV. From a study of Fe-Mn Stadeler (*C. A.* 2, 2927; *Metallurgie* 1909, 3) found that Mn combines with C to give Mn₃C

(6.72% C) and this compd. is endothermic like Fe_3C and very stable at the temp. of cementation. This fact is discussed in some detail and it is thus shown that the behavior of IV does not contradict the general interpretation of the 1st phase of cementation that is developed at some length at the beginning of this paper. IV. Cementation of copper by means of ferro-aluminium. *Ibid* 245-50.—The Al bronzes are increasing in industrial importance because of their mechanical properties (resembling mild steel), their color and luster and their resistance to chem. action. It was therefore of interest to det. if they could be obtained by migration of Al into Cu or its alloys. Test expts. by the method previously used (*C. A.* 16, 1063) with Cu bars packed in commercial Al mixed with wood charcoal at temps. (550°) below the m. p. of Al for 72 hrs. showed a practically negligible cementation. On the basis of the earlier results on cementation of Cu with Fe-Mn in which practically no migration of Fe occurred it seemed advisable to try Fe-Al. Gwyer (*C. A.* 2, 1819) studied the system Fe-Al and found a compd. Al_2Fe (40% Al). With this compd. the temp. of cementation could be increased above the m. p. of Al. This alloy (39.70% Fe, 54.40% Al, C 0.49%) was ground and prepd. as usual with 5% charcoal and heated with Cu bars (99.81% Cu) as before at 250° for 72 hrs. The Al content of the 4 outer layers (0.1 mm. thick) taken from the bars was 5.7, 3.5, 1.7, and 0.31%, resp. Sections show that the Al appears to be taken up by the Cu crystals with which it forms mixed crystals. The results of these preliminary expts. are to be extended.

E. J. WITZEMANN

X-ray examination of the inner structure of strained metals. I. Chiefly on copper wires. AKIMASA ONO. *Mem. Coll. Eng. Kyushu Imp. Univ.* 2, 241-60 (1922).—Strained metals, chiefly Cu wires, and also some specimens annealed after straining give X-ray interference figures showing 6 bands radiating from the central spot. Thus the crystal lattices form a fibrous structure in the pulled or drawn state. By finding the inclinations of several simple planes in the face-centered lattice, and calcg. the relative intensities of rays reflected by the planes it is found that the trigonal axis coincides with the longitudinal or fiber direction of the specimen. The figure obtained from the material annealed after straining shows numerous spots indicating the growth of individual crystals by aggregation. The change in lattice structure upon straining is considered as the explanation of other changes in properties observed in strained metals. Remarkably beautiful photographs of the interference figures are given.

G. L. CLARK

The influence of the rate of cooling on the hardness and microstructure of eutectic mixtures. N. S. KURNAKOV AND A. N. ACHNASAROV. *Z. anorg. allgem. Chem.* 125, 185-206 (1922).—Eutectics of Cd-Ag, Ag-Cu, Au-Ni and Sb-Zn were studied. The eutectic possesses the greatest capability for hardness and increase of hardness by rapid cooling. The increase in hardness is directly proportional to the velocity of solidification, the rate of cooling from high temps. and the degree of fineness of the individual crystals. Increased hardness in eutectic alloys produces brittleness and increases the time required for etching. The rate of cooling has no effect upon the hardness of the solid soln. alloys. No photomicrographs are given. W. A. MUDGE

Constitutional diagram of the iron-carbon-tungsten system. SIGEAKI OZAWA. *Sci. Repts. Tohoku Imp. Univ.* 11, 333-50 (1922).—The constitutional diagram of the Fe-W system is detd. By the addition of W, the temp. of crystn. of Fe-W alloys is not so much affected as shown by Harkort's results. It is dilatometrically ascertained that the A_2 point rises with the increase of W, but its intensity gradually diminishes. The A_2 point, 790° , is not sensibly affected by the addition of W. The investigation of the microstructure of the system leads to the same result as that of Honda and Murakami. There is only 1 compd. existing between Fe and W, viz., Fe_3W . The constitutional diagram of the Fe-C-W system has been studied by thermal and magnetic analysis

and by microscopic examn. From magnetic and microscopic investigation, it has been ascertained that the cementite and tungstide are mutually sol. to a certain concn., and that in high-C and W steels, these solid solns. decompose giving out WC. The ternary eutectic point has been detd. to be 1065° , its compn. being 15.0 W, 3.6 C, and 81.4% Fe. The binary eutectics of austenite-cementite and austenite-tungstide, which meet at the ternary eutectic point above stated, have been found by thermal analysis and from the microstructure.

V. O. HOMERBERG

Equilibrium diagram of the copper-zinc system. HIROSHI IMAI. *Sci. Repts. Tohoku Imp. Univ.* 11, 313-32(1922).—The equil. diagram of the Cu-Zn system has been obtained chiefly by means of the elec. resistance measurement. It nearly coincides with Shepherds' and Tafel's diagram. As to the transformation of the β -constituent, a negative result is obtained for the eutectoid sepn. or an allotropic change. The elec. resistance method and the X-ray analysis lead to a new result, viz., that the transformation point at 480° is the beginning point during cooling, and the ending point during heating, of a progressive change of non-allotropic nature, extending from a low temp. to 480° . The change is of the same nature as the A_1 transformation in Fe. The γ -constituent has also a transformation at 480° and another transformation at 260° of the same nature as that in the β -constituent. Soly. lines have been detd. in the field of α , β , and γ at high temps. The freezing ranges have been detd. by the elec. resistance method. They are somewhat narrower in the compn. of the β -constituent than those previously detd. by thermal analysis, especially in the compn. of 60/40 brass, the freezing range approaching almost 0. The resistance-compn. curves at room temp., and solidus and liquidus lines have been obtained. The δ -constituent dissociates into a eutectoid mixt. at 530° .

V. O. HOMERBERG

Recrystallization. E. O. COURTMAN. Brit. Non-Ferrous Metals Research Assoc., *Bull.* No. 8, 6-15(1923).—An idea is given of the character of the investigations which have been carried out on the recrystn. of non-ferrous metals and alloys.

V. O. H.

Radiography of metals. H. H. LESTER. *Army Ordnance* 3, 210-15(1923).—The technic of the radiographic testing of metals and its applications are considered. Radiographs are included.

V. O. HOMERBERG

Fatigue or progressive failure of metals under repeated stress. H. F. MOORE, J. B. KOMMERS and T. M. JASPER. *Proc. Am. Soc. Testing Materials* 22, II, 266-311(1922); cf. C. A. 16, 228, 890, 1382, 4166.

R. S. W.

Observations on the occurrence of iron and silicon in aluminium. E. H. DIX, JR. *Trans. Am. Inst. Mining Met. Eng.* 1923, No. 1213-N, 14 pp.—The various structures found in commercial Al contg. the usual Fe and Si impurities are illustrated in detail. The characteristic forms of the FeAl₃-Al eutectic, of the Si-Al eutectic, and of the ternary eutectic of Si, constituent X, and Al, are shown by a series of photomicrographs. The constituent X often takes the same form as FeAl₃, and cannot be distinguished except by careful examn. A method of etching to aid in differentiating between these 2 constituents is cited.

V. O. HOMERBERG

Bright annealing of copper wire in an atmosphere of natural gas. P. F. DEMMLER. *Trans. Am. Inst. Mining Met. Eng.* 1923, No. 1215-N, 4 pp.—In annealing spools of hard-drawn Cu wire in an atm. of natural gas at a temp. of 350° , the outer layers of wire on each spool were dark in color and did not present the desired bright appearance. The trouble was due to the presence of traces of O in the gas; passing the gas over Cu heated to 600° before passing it into the annealing chamber prevented any coloring of the wire.

V. O. HOMERBERG

A study of bearing metals. C. H. BIERBAUM. *Chem. Met. Eng.* 28, 304-8(1923); *Trans. Am. Inst. Mining Met. Eng.* 1923, No. 1216-N, 12 pp.—It is well established that bearing metals must be composed of an intimate mixt. of soft and hard crystals;

the term hard is used to express the capacity for resisting cutting or abrasion. For most satisfactory bearing service, the physical properties of the journal bear some relation to the bearing metal, as for best service requirements the bearing and journal must polish each other. Therefore the hardest crystal in the bearing metal must bear some relation to the hardest crystal in the journal. An instrument is described by means of which the hardness of the individual crystals can be detd. V. O. H.

Determination of the coefficient of normal viscosity of metals. KOTARO HONDA ANN SEIBEI KONNO. *Sci. Repts. Tohoku Imp. Univ.* 11, 435-45(1922).—The coeffs. of normal viscosity of 12 different metals are measured at room temp.; the values range from 0.7×10^8 to 27×10^8 . The coeff. of the viscosity of a metal having a lower m. p. is large. The coeff. of normal viscosity is of the same order of magnitude as that of tangential viscosity. Annealing causes the diminution of the coeff. of viscosity. In C steels, the coeff. of viscosity increases with the content of C. V. O. HOMERBERG

Contribution to the knowledge of tempering. P. OBERHOFFER AND J. WELTER. *Stahl u. Eisen* 43, 105-10(1923).—The influence of compn. (especially S), temp., time of heating, and tempering medium upon the impact properties of cast Fe. 60 hrs. at 900° gave best results. An increase in S lowers impact values. Mn acts similarly to S, although 1/4 as powerful. Low-S Fe heated in Fe_2O_3 picks up S; high-S Fe under similar conditions loses S. Photomicrographs show typical structures. W. A. M.

Carhonex case-hardening compounds. ANON. *Engineering* 114, 532(1922).—Carhonex is a case-hardening compd. that is in paste form. Its uses and advantages are discussed. V. O. HOMERBERG

New method for case hardening. FRANK HODSON. *Chem. Met. Eng.* 28, 308 (1923).—The CO in the gas in the carburizing pots is materially increased by means of a catalyzer. The advantages in the use of the method are enumerated. V. O. H.

Structure of chromium-nickel steel. H. B. PULSIFER AND O. V. GREENE. *Chem. Met. Eng.* 28, 354-6(1923).—Micrographs fail to show any change in structure in quenched Cr-Ni steel after various draws, despite large differences in physical properties. Precautions are given for etching and photographing. V. O. HOMERBERG

Magnetic change A_2 in silicon and chromium steels. HOWARD SCOTT. *Chem. Met. Eng.* 28, 212-5(1923).—It is impossible to rely upon the loss of magnetism to indicate proper hardening temps. for these steels, since the C change point is at a higher temp. than the magnetic change point. V. O. HOMERBERG

Low-temperature brittleness in silicon steels. N. B. PILLING. *Trans. Am. Inst. Mining Met. Eng.* 1923, No. 1220-S, 10 pp.—The brittleness of Si steel is an inherent property of Fe, modified by the alloyed Si. Commercial Si steel becomes brittle when the Si content exceeds 4.2%. Temporary ductility may be obtained by carrying on cutting or deformational operations at temps. slightly above atm., the temp. depending on the steel compn. Brittleness is only slightly modified by heat treatment. The purest Fe shows a similar brittleness at about -130°. Si and Al raise, and Mn lowers the critical ductility temp. V. O. HOMERBERG

Influence of temperature, time and rate of cooling on physical properties of carbon steel. H. M. HOWE, F. B. FOLEY AND JOS. WINLOCK. *Trans. Am. Inst. Mining Met. Eng.* 1923, No. 1226-S, 47 pp.—Steels of 0.34, 0.52 and 0.75 % C were subjected to various temps. above A_{c1} , held for 10, 60, and 120 min. and cooled at various rates; then their tensile properties, hardness, and resistance to impact were compared. 0.52% C steel was quenched in H_2O from different temps. above A_{c1} and drawn at a number of temps. below A_{c1} . The same steel was subjected to repeated heatings and the physical properties were detd. The specimens were treated in 1/4-in. round sections. V. O. HOMERBERG

Cause of the origin of a constant force during tensile tests of soft steel. CHARLES

FREMONT. *Compt. rend.* **176**, 361-4(1923).—In the tensile strength of soft steels, a point is reached at the elastic limit where the specimen undergoes a continued, permanent extension without increase in the applied force. Photographs show the development of two types of slip planes which progress locally along the specimen. The force remains const. until these local deformations are thus completed. G. R. FONDA

X-ray examination of steel castings. H. H. LESTER. *Chem. Met. Eng.* **28**, 261-7 (1923).—It is possible to locate $1/16$ in. flaws in steel 3 in. thick with a 30-min. exposure from commercial X-ray tubes. Correspondingly smaller defects can be likewise revealed in thinner sections. V. O. HOMERBERG

Determination of the fatigue-resisting capacity of steel under alternating stress. T. ROBSON. *Engineering* **115**, 67-8(1923). V. O. HOMERBERG

Magnetic study of some heat-treated carbon steels. E. D. CAMPBELL and E. R. JOHNSON. *J. Iron Steel Inst.* advance proof, **1922**, 22 pp.—Further expl. evidence is given in support of the hypothesis of the mechanism of permanent magnetism in bar magnets embodied in a paper submitted by C. to the Faraday Soc. in July 1920. This hypothesis states that the force fields existing at the poles of a bar magnet represent the cumulative effect resulting from the serial alignment of the poles of the force fields of carbides or other solutes in soln. V. O. HOMERBERG

Heat treatment of steel castings. H. C. INSEN. *Blast Furnace Steel Plant* **11**, 95-9(1923).—The characteristics of steel castings in the raw and in the thermally treated condition are considered. A consideration of the correct treatment with relation to size and compn. of casting is given. V. O. HOMERBERG

Ingot corner segregation in a nickel chrome steel. T. H. TURNER. *Engineering* **114**, 662-4(1922).—The steel was cast in an octagonal ingot mold. The segregation was mainly MnS. Planes of segregation should be avoided by the use of new mold shapes, better regulated pouring rates and temps., or even by centrifugal casting. The elimination of danger from such segregation may be possible by the use of special methods of forging and machining. The user may always detect such defects by S prints and mech. tests taken so as to cut across the material which originally formed ingot corners. V. O. HOMERBERG

Bibliography of high-speed tool steels. ANON. *Trans. Am. Soc. Steel Treating* **3**, 47-89(1922).—A complete digest from 29 technical magazines and many books covering the period 1900-22. W. A. MUDGE

The chemical properties of alloys. G. TAMMANN. *Z. Metallkunde* **13**, 406-19 (1921).—The phys. properties of binary alloys of 2 metals that form a continuous series of mixed crystals change regularly with varying compn., whereas their chem. properties alter suddenly when the atomic ratio of the metals present exceeds a certain well defined limit, which may generally be expressed as $n/8$, where n , usually 1, 2, 4, 6, 7, rarely 3 or 5, is the number of atoms of the more noble metal in every 8 metal atoms. Thus, $(\text{NH}_4)_2\text{S}_2$ blackens, in the cold, all alloys of Au and Cu contg. less than 50.8% of Au (atomic ratio 2/8 Au), while those richer in Au remain un tarnished even after 4 yrs.' immersion. Again, HNO_3 dissolves Ag completely from Au-Ag alloys contg. less than 52.5% of Au (atomic ratio 3/8 Au), partly from those contg. 52.5-64.4% of Au (atomic ratio 4/8 Au), and not at all from those still richer in Au. Under certain conditions, however, these limits disappear, that is, the atoms of the active component tend to diffuse towards the surface, so that the surface layer falls below the limiting value. H_2S attacks Cu-Au alloys richer in Au as the temp. rises, until, at 140° it blackens Au contg. only 1% of Cu. A theoretical explanation of the above phenomena, based on the space-lattice theory of crystal structure, is given in some detail and it is shown that it is possible to prep. what may be called "space-lattice isomerides" of alloys which behave differently towards certain reagents. The electrochem. behavior of

binary alloys may be studied by measuring the e. m. f. of cells in which the electrolyte consists of a salt of the more electronegative metal from which one pole is made, while the other pole consists of different alloys of the 2 metals. If the compn. of the latter is plotted against the voltage of the cell, the curve obtained for alloys in which inner diffusion takes place (*e. g.*, amalgams) resembles a hyperbola concave to the axis of compn. while that obtained for alloys of metals (*e. g.*, Cu-Mn) which form a continuous series of mixed crystals, in general, runs close to this axis until a certain definite compn. is reached, when it rises in a nearly perpendicular straight line to a const. voltage equal to that of a cell in which the poles consist of the 2 pure metals. In alloys of Au with Cu and Ag the curve rises after a certain percentage of Au, in a straight line to the value for pure Au. This is probably due to the deposition of a fine film of the latter on the surface of the alloy. Two metals that form several series of mixed crystals give alloys that yield similar curves except that there are a number of steps corresponding with the various series of mixed crystals, but these steps do not correspond with any definite atomic ratio between the elements. Au-Cu alloys, when made the anode in an electrolytic cell contg. a soln. of $\text{Cu}(\text{NO}_3)_2$, are attacked without evolution of O if the Au does not exceed 29 atoms % Cu dissolving from the alloy. If the voltage applied to a cell contg. a large Cu cathode and a small anode of Au-Cu alloy is plotted against the ampere the curves for alloys contg. 25-28 atoms % of Au show a peculiar double hump, whereas the curves for alloys richer or poorer in Au are roughly parabolic. The decompn. voltage of the series is at a max. at nearly the same limit as that at which there is no attack by reagents, namely, 27 atoms % of Au, while polarization is first noticeable with alloys contg. 50 atoms % of Au. Alloys contg. more Au behave in these two cases like pure Au.

J. C. S.

Alloys of aluminium with iron. N. KURNAKOV, G. URASOV AND A. GRIGORJEV. *Z. anorg. allgem. Chem.* 125, 207-27 (1922).—A study of the Al-Fe system giving data of thermal-analyses, elec. cond., and microstructure. Al is sol. both in α and γ Fe. 0-39.7% Fe shows δ + eutectic. Al_2Fe_3 is the only compd. formed. This occurs at 40% Fe and is endothermic. Elec. cond. decreases rapidly from pure Al to Al_2Fe_3 , is const. to 52.1% Fe, rises sharply to a max. at 65% Fe, decreases, passing through a minimum at 79.1% Fe, and rises sharply to pure Fe. These results differ from those of Gwyer and Guillet. The equil. diagram is revised to correspond with the exptl. data. No photomicrographs are given.

W. A. MUDGE

Preparation of light aluminium-copper casting alloys. R. J. ANDERSON. *Bur. of Mines, Tech. Paper* 287, 44 pp. (1922).—Al alloy foundries employ 3 methods for the introduction of Cu into Al in making light Al-Cu alloys: (1) the use of pure Cu directly, (2) the use of a 33:67 Cu-Al alloy, and (3) the use of 50:50 Cu-Al alloy. The usual method of prepg. rich alloys is to melt the Cu and part of the Al separately and then to pour the Cu into the Al, keeping the temp. as low as possible by adding the remainder of the cold Al. A suitable method for prepg. rich alloys on a large scale is described in detail. Expts. in the prepn. of the rich alloys and in the 92:8 Al-Cu alloy (No. 12 alloy) have yielded data with regard to dress losses, relative costs, and the merits of different methods. The various methods used at different foundries have been compared in the light of the figures obtained from the expts. and of views expressed by representative foundrymen. Many believe that the most desirable method of prepg. No. 12 alloy is by the addn. of light Cu sheet or small punchings to the liquid Al. This method saves making the Cu-rich alloy. The resulting castings run with an uneven Cu content; hence they are hard or soft, owing to the uneven distribution of CuAl_2 formed in the alloy, unless the melt is thoroughly and often stirred. The danger of segregation may be minimized by the use of Cu-rich alloys for introducing the Cu into the Al-Cu alloy. A small foundry can use the direct Cu method to advantage but a larger foundry

is at a disadvantage owing to difficulties at times in obtaining pure Cu, in the unskilled labor usually employed, and the usual desire to hasten production during rush periods. The No. 12 alloy can be prepd. conveniently and economically by charging the Alingot, No. 12 alloy pig or scrap, and the Cu-rich alloy together into the melting furnace. No advantage is apparently gained by any other process.

R. F. PERKINS

The use of non-ferrous alloys under superheat. H. C. DEWS. *Engineering* 114, 541-2(1922).—The use of Cu, 70/30 brass, 60/40 brass, admiralty gun metal and rolled cupro-Ni is considered. Curves are given to show change in phys. properties with increase in temp.

V. O. HOMERBERG

Binary lead alloys. J. GOEBEL. *Z. Metallkunde* 14, 449-55(1922); cf. C. A. 17, 52, 719.—Na is a much better hardening agent for Pb than Cd, As, Sn, Hg, or Bi up to the limit of solid soln. 0.8% Na gives the hardest alloy, which is four times as hard as any other investigated. At 10% Na is inferior only to As, Sb, and Cd as a hardening agent. The elec. cond. is a linear function of compn. up to the limit of the solid soln.; when a compd. is formed the elec. cond. falls continuously on increase of Na and passes through a low minimum. The relation between sp. gr., hardness, and elec. cond. is discussed as a function of chem. compn. A bibliography is given. W. A. M.

Effect of magnetic fields on the resistivity of some alloys. J. OYATA. *Res. Electrotech. Lab. Tokyo* No. 101, 20 pp.(1921); *Science Abstracts* 25A, 618.—The application of the electron theory to elec. conduction in pure metals when subjected to a transverse magnetic field shows that the relative change in resistance is made up of two terms, one due to change in mol. configuration, the other due to electronic drift. The latter term is absent in the expression for the longitudinal field. In the case of alloys, the term depending on mol. configuration would be further influenced by a magnetic field. The alloys investigated include constantan, manganin, eureka, platinoïd, Cu-Mn, Cu-Mn-Al, phosphor-bronze, Pt-Ir, and nichrome, and the change of resistance was measured in both longitudinal and transverse fields (up to 20,000 c. g. s. units) and at various temps. between that of liquid air and steam. The resistance detns. could be made in the most favorable cases to 1 part in 1,000,000, and tests on Ni, Au, and Cu were in substantial agreement with those of previous observers. In Cu alloys contg. Ni or Mn, both transverse and longitudinal fields diminish the resistance, and the effect observed always decreases with rise of temp. It would appear that in these cases the field produces an increase in the free path of the conducting electron. For weak fields the decrease is proportional to the square of the field. In phosphor-bronze and Pt-Ir the effect is very small, and is probably due to the presence of magnetic constituents. In nichrome the effects are very similar to those for pure Ni, and some part of the Ni exists in the free state in this alloy.

H. G.

Density determination of metals and alloys at high temperature with special consideration of the molten state. IV. Measurements according to the buoyancy method. The binary systems antimony-tin and antimony-aluminium, and the metals silver and magnesium. F. SAUERWALD. *Z. Metallkunde* 14, 457-61(1922); cf. C. A. 16, 3844.—The deviation of sp. vol. from the rule of mixt. for the Sb-Zn alloys in the molten condition, as well as at high temps., is due to Zn_2Sb_2 which exists in the molten alloys. The sp. vols. of all Sb-Zn alloys over the temp. range 20-800° show a max. between 35 and 75% Sb. The variation in expansion of the solid Al-Sb alloys observed at high temps. was not found in the fluid state. The almost complete decompn. of the compd. AlSb, beginning at 940°, together with other facts indicates the necessity for a revision of the equil. diagram; a temporary revision is offered. The sp. vol. of solid and molten silver is a linear function up to 900° and then rises sharply to 1100°. Arguments are given in support of the use of magnesia crucibles in this work as containers for the NaCl-KCl salt bath. The sp. vol. of Mg at 780° is 0.566. W. A. M.

How arsenic affects alloys. H. J. ROAST AND C. F. PASCOE. *Foundry* 51, 67-70 (1923).—A comparison is made between Sb-Pb alloys contg. As and other bearing metals. The former are better in maintaining their hardness as the temp. rises.

V. O. HOMERBERG

Cold-rolling and reheating of copper-zinc alloys. P. J. H. WIELAND. *Mitt. Kaiser Wilhelm Inst. Eisenforschung* 3, 1(1922); *Science Abstracts* 25B, 481-2.—Summary of mech. and metallographic tests of Cu alloys rich in zinc contg. 25, 37, 40% of zinc. II. G.

Dial copper and 12 percent watch nickel. WM. B. PRICE. *Metal Ind.* 21, 11-2 (1923).—A description is given of the manuf. of these products from the raw material to the finished product.

V. O. HOMERBERG

Acid-resisting metal unique. H. E. DILLER. *Foundry* 51, 47-52(1923).—Castings made of high-Si Fe melted and remelted in an air furnace with the addn. of 50% Fe-Si. The metal is hard and brittle, easily welded, but not machineable. V. O. H.

Further growth of metal crystals by sepn. from the gaseous phase (KOREF) 2. Apparatus for photomicrography (DURANTE) 1. Atmospheric pollution by industrial wastes (SWAN) 13.

BELATREV, N. T.: *Crystallization of Metals*. London: University of London Press, Ltd., 143 pp. 7s. 6d.

GOLDSCHMIDT, V. M.: *On fremstilling av bariumlegeringer*. Kristiana: A. Aschehoug & Co. 36 pp.

GUILLET, LÉON: *Alloys: Les méthodes d'étude des alliages métalliques*. Paris: Dunod. 503 pp. F. 65.

KLAMER, TH. H.: *Het kleuren van metalen. Een beknopt handboekje voor metaalbewerkers en voor allen, die in de versierings-techniek van metalen werkzaam zijn*. Deventer: Ae. E. Kluwer. 138 pp. Fl. 2.50, bound, 3.50.

KRUPP A.: *Die Legierungen*. 4th Ed. revised and enlarged. Vienna and Leipzig: A. Hartleben. 501 pp. M 120.

LEBRUN, MAURICE: *Soudure et découpage des métaux par l'arc électrique*. Paris: Gauthier-Villars et Cie. 43 pp. Fr. 3.50

Mineral flotation. J. F. MYERS. U. S. 1,446,314, Feb. 20. A mineral pulp, e. g., "Hanover dust" of Zn ore, is treated with a hydrogel of Cu before flotation, in order to promote the flotation sepn.

Mineral froth-flotation. W. O. BORCHERT. U. S. 1,445,989, Feb. 20. Colloidal substances are sepd. from ore pulps by a preliminary froth-flotation and the mineral substances remaining are then subjected to a further flotation sepn.

Concentrating oxidized ores. W. O. BORCHERT. U. S. 1,446,375, Feb. 20. Oxidized ores contg. sufficient colloidal substances to inhibit effective sulfidization and flotation sepn. of oxidized metallic values, e. g., compds. of Cu, Zn and Pb, are preliminarily freed from the deleterious proportion of colloidal substances, e. g., by addition of Na silicate and gravity sepn., and are then sulfidized and subjected to flotation sepn.

Selective mineral flotation controlled by colloids. W. O. BORCHERT. U. S. 1,446,376, Feb. 20. Differential flotation of mineral constituents such as sulfides of Pb and Zn is effected by adding to the mineral pulp (initially free from interfering colloids) a small amt. of clay or other colloidal material which will inhibit the flotation of one constituent, e. g., ZnS, while permitting the flotation of the other, e. g., PbS. The colloid may then be removed to permit flotation of the second component.

Filtering ore pulp containing colloidal substances. W. O. BORCHERT. U. S. 1,446,378, Feb. 20. Normally flocculated colloidal matter is dispersed in ore pulps

by Na silicate, gum arabic, etc., and the material is sepd. from the dispersed colloidal matter by gravity sufficiently to permit its more ready filtration.

Mineral concentration. W. O. BORCHERT. U. S. 1,446,377, Feb. 20. A mineral concentrate contg. colloidal constituents is subjected to a deflocculation and dispersion to facilitate sepn. of the mineral constituents from the dispersed colloidal material, and the materials are then subjected to a regulated settling which effects sepn. of the bulk of the colloidal materials and H_2O from the mineral constituents which are capable of settling out.

Concentrating ores with oily reagents. L. M. BARKER. U. S. 1,447,006, Feb. 27. In pneumatic flotation of minerals with oily reagents, the ore pulp is brought into contact with oily substance while the latter is carried as a thin liquid film on an 18-mesh screen or other finely reticulated material.

Recovering sulfides from emulsions. B. HUNT. U. S. 1,446,307, Feb. 20. Ore products from hydrometallurgical operations, or similar material contg. metallic sulfides together with S or to which S has been added together with gang or the like wetted with H_2O , is heated to a temp. above the m. p. of S under pressure and agitated to effect coalescence of the sulfide and S particles so that they may be sepd.

Recovering values from tinned-iron wastes. H. V. WELCH and W. A. SHREK. U. S. 1,446,953, Feb. 27. Tinned Fe waste is heated in a reducing atm. while passing hot gases in contact with it at sufficient temp. and in sufficient vol. to distill off the Sn. The residue of Fe is then fused.

Metallurgical furnace. J. H. GRAY. U. S. 1,445,679, Feb. 20. The furnace has a slag pocket with a vertically movable bottom so that it may be gradually lowered to permit the slag to solidify in a large mass before removal.

Reversible regenerative open-hearth furnace. T. T. SCOTT. U. S. 1,446,072, Feb. 20.

Open-hearth furnace. E. A. WHEATON. U. S. 1,446,077, Feb. 20. The pat. relates to the wall and roof structure of the furnace.

Oxygenated blast for metallurgical furnaces. M. H. ROBERTS and C. C. VAN NUYS. U. S. 1,445,973, Feb. 20. Air for the blast is liquefied with enrichment in O, by rejection of an unliquefied portion rich in N, and the blast is derived from the O-enriched fraction.

Operation of copper-matting furnaces. H. H. SROUT. U. S. 1,445,980, Feb. 20. In the operation of a Cu-matting furnace, a flame is propagated over substantially the entire area of the firing end of the furnace between the slag line and arch, in order to operate the furnace with good capacity.

Reversible gas-fired furnace for melting metals. W. LÜTZ. U. S. 1,445,225, Feb. 13.

High-speed steel. W. B. BROOKFIELD. U. S. 1,446,153, Feb. 20. Ingredients of high-speed steel such as finished ingots contg. all the metals are heated together in successive stages to produce increasing homogeneity of the ingredients and assimilation into a uniform compn. The preliminary heating for casting the ingots may be followed by a further melting treatment at a lower temp. to insure uniform assimilation of the constituents.

Resistance alloy. J. H. WHITE. U. S. 1,445,253, Feb. 13. An alloy for elec. resistances, e. g., for heating app., is formed of Fe 11%, Ni 75%, and Ta (or "tantalum-columbium") 14%.

Steel alloy. H. S. FOOTE. U. S. 1,446,497, Feb. 27. Steel is alloyed with Si 0.1-0.8, Mn 0.20-1, U 0.1-0.9 and V 0.1-0.9%. An alloy of this compn. is non-brittle and is adapted for making springs or machine parts.

Heat-treating bronze alloy. J. W. BRANWELL. U. S. 1,446,332, Feb. 20. A

bronze alloy which contains Cu 85% or more, Sn 9.5% or more and Zn 2% or more, and which may also contain small amts. of Al, As, B, Co, Mg, Mn, Mo, Ni, P, K, Si, Ti, W, U, V or Zr, is heated to 500–860°, immediately quenched in cold H₂O and then compacted by rolling, drawing or swaging, to adapt it for manuf. of bushings.

Composite castings including copper and ferrous metal. C. T. WILKS. U. S. 1,446,678, Feb. 27. A molten Cu alloy (free from Zn) is poured into a mold and permitted to come to a semi-molten state in the bottom of the mold. Molten Fe, semi-steel or steel is then poured on the Cu alloy to fill the mold.

Locally annealing metal plates. R. S. SMITH and R. STRESAU. U. S. 1,446,354, Feb. 20. Metal plates, *e. g.*, automobile frame bars, are intermittently fed in succession into a heating zone where the parts to be annealed are locally heat-treated.

Tinning and galvanizing apparatus. L. JONES. U. S. 1,446,506, Feb. 27. A tinning pot machine is provided with tinning rolls and cleaning brushes for the rolls.

10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER

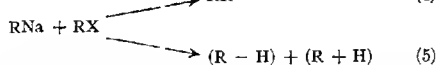
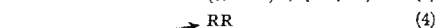
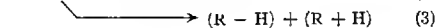
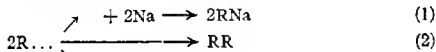
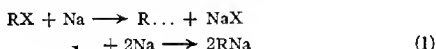
Valency theories of organic chemistry. F. HENRICH. *Jahrb. Radioaktiv. Elektronik* 19, 1–38(1922).—An historical account of the theory of valency leading up to a discussion of the modern views of Kossel, Hinsberg, J. Stark, Pauli, and Vorländer on the valency of org. compds. J. C. S.

Recent advances in science—Organic chemistry. O. L. BRADY. *Science Progress* 17, 199–204(1922).—Review of recent work on the photosynthesis of nitrogenous compds. from nitrates and CO₂, and on the constitution and synthesis of *laudanine*.

JOSEPH S. HEPBURN

Metallo-organic compounds. III. Mechanism of the Wurtz-Fittig synthesis. H. H. SCHLUBACH and E. C. GOES. *Ber.* 55B, 2889–902(1922); cf. *C. A.* 14, 1983.—S. and G. have made use of the property of Na alkyls of absorbing CO with formation of ketones and tert. alcs. to det. whether, as has been assumed by various investigators, Na alkyls are intermediate products in the Wurtz-Fittig synthesis. As a matter of fact, PhBr in C₆H₆ shaken with Na in an atm. of dry CO vigorously absorbs the CO after a short time and yields the same products (Ph₂CO, Ph₂COH and BzOH) as are obtained from PhNa and CO. In the analogous action of CO on EtBr and Na in Et₂O the absorption of the CO cannot be followed so clearly, for gaseous products are formed as well as liquid ones, but the characteristic end products, Et₂CO and Et₂COH, can be detected in this case also. A further direct proof of the intermediate formation of Na alkyls is afforded by the fact that bright Na shavings covered with PhCH₂Cl first assume the wine-red color characteristic of PhCH₂Na and only afterwards change slowly into the dark blue substance which usually is formed in all W.-F. syntheses. These results, in connection with the observations of Acree (*Am. Chem. J.* 29, 588(1903)) and of Shorin (*C. A.* 4, 2814), indicate with certainty that the normal W.-F. synthesis proceeds according to the scheme $RX + 2Na \longrightarrow RNa + NaX$ and $RNa + RX \longrightarrow R_2 + NaX$. The "normal" reaction is always accompanied, in many cases almost completely displaced, by side reactions. With aliphatic alkyl halides, unsatd. hydrocarbons are formed along with the normal products. As found by Acree and confirmed by S. and G., PhNa and EtBr give not only PhEt but also C₆H₅ + C₆H₆, *i. e.*, one residue (Et) gives up, the other (Ph) takes up H. This migration of the H leads to the assumption that the residues exist transiently as free radicals and are then "disproportioned" (*disproportioniert*) into C₆H₅ and C₆H₆. The primary process, therefore, consists in the splitting off of a H atom; and the ease with which this occurs apparently varies greatly with different radicals. Corresponding to the slight mobility of the H atoms in C₆H₆, Ph splits off a

H atom only with relative difficulty and the triarylmethyls therefore do not easily undergo disproportionation, while the lower members of the aliphatic series, from Et up, show a strong tendency in this direction. The only exception is Me, which has but slight tendency to pass over into CH₃; MeI and Na give only C₂H₆ and no C₂H₄. Substituted methyls, however, have a loosely held H atom and PhCH₃ shows a distinct tendency to pass into PhCH or its polymer, PhCH:CHPh. The H which is split off is in general taken up by the radicals which have not yet been decompd. and if other easily reducible substances are present they may serve as acceptors for the H. Shorin obtained an impure PhEtCHOH (probably contg. PhCH₂OH also) by the action of EtNa on BzH, and S. and G., using a higher boiling solvent (PhMc), have confirmed his observation and, furthermore, by collecting the C₂H₄ evolved, have shown that H is split off under these conditions. If this tendency to split off H, then, is the cause of the side reactions, it is also the factor which det. the yield of normal products in the W.-F. synthesis. A mixt. of RBr, R'Br and Na gives approx. equimol. amts. of RR, R'R' and RR' when R and R' are closely related aliphatic residues, but almost exclusively RR' when R = Et and R' = Ph. Why practically only EtPh is formed in the latter case can be explained by means of the CO reaction; when equimol. amts. of EtBr and PhBr are shaken with Na in a CO atm., the vigorous absorption of gas shows that the reaction does not proceed appreciably according to the scheme $2\text{EtBr} + 2\text{Na} \longrightarrow \text{Et}_2 + 2\text{NaBr}$, for otherwise the gaseous Et₂ would be liberated, and on working up the product there are obtained only Ph₂CO, Ph₂COH and BzOH (the products of the action of CO on PhNa), and no Et₂CO and Et₂COH (the products of the action of CO on EtNa). Under the same conditions, therefore, PhNa is formed much more readily than EtNa. On the other hand, the PhNa so formed reacts much more rapidly with the EtBr than with the PhBr, thus giving PhEt. The formation of the Na alkyls from the alkyl halides can be explained in the same way as the anomalous course of the reaction between alkyl halides and Na alkyls described above, viz., by assuming the intermediate existence of free radicals: $\text{RX} + \text{Na} \longrightarrow \text{R}\cdot + \text{NaX}$ and $\text{R}\cdot + \text{Na} \longrightarrow \text{RNa}$. If the radicals thus set free have the property of easily splitting off a H atom, the disproportionation mentioned above may naturally occur in this first phase. The W.-F. synthesis may therefore be represented by the following general scheme:



The Na alkyl may also react with the solvent (*e. g.*, Et₂O, C₆H₆) and with the C₆H₅ nucleus of aromatic alkyl halides and thus introduce complications. That the blue products usually formed in the W.-F. synthesis are inorg., as concluded by Shorin, has been confirmed by a study of that obtained with PhCH₂Cl and Na, which was found to be NaCl. S. and G. agree with the view of Späth (*C. A.* 8, 503) that the first phase in the action of alkyl halides on Grignard compds. consists in the formation of free alkyls and believe that this explanation can be applied to the other anomalous reactions (such as the reducing action, etc.) of these compds. C. A. R.

γ-Methyl-Δ⁷-pentene. HORTENSE VAN RISSEGHEN. *Bull. soc. chim. Belg.* 31, 213-22(1922).—Dehydration of MeEt₃COH by means of *p*-MeC₆H₄SO₃H yields a mixt. of the 2 stereoisomeric γ-methyl-Δ⁷-pentenes which may be sepd. by fractional

distn. The following phys. consts. were detd.: for the fraction b. 65.1–5.7°, d_{15}^4 0.7220, $n_{\text{H}_2\text{O}}^{15}$ 1.3974, $n_{\text{H}_2\text{O}}^{15}$ 1.4058, $n_{\text{H}_2\text{O}}^{16}$ 1.4108, $n_{\text{H}_2\text{O}}^{16}$ 1.3997; for the fraction b. 69.9–70.2°, d_{15}^4 0.7022, $n_{\text{H}_2\text{O}}^{15}$ 1.4047, $n_{\text{H}_2\text{O}}^{15}$ 1.4136, $n_{\text{H}_2\text{O}}^{16}$ 1.4186, $n_{\text{H}_2\text{O}}^{16}$ 1.4072. It is claimed that this is the 1st sepn. of isomeric ethylenic hydrocarbons that has been effected. Both substances are transformed into MeCOEt on oxidation with CrO_3 . The action of Br on each is merely additive, but aq. HCl acts on the fraction of lower b. p. as an isomerizing agent. Like other ethylenic substances, these hexenes undergo spontaneous oxidation with formation primarily of peroxides and subsequently of aldehydic substances.

J. C. S.

Synthetic experiments with ethynylcarbinols. I. Transformation of 3-methylbutinol into 3-methylbutenin, 3-methylbutanolone and its condensation products. HELMUT SCHEIBLER AND ARTUR FISCHER. *Ber.* 55B, 2903–23(1922).—In the course of investigations on artificial rubber there has been devised a synthesis of isoprene from 3-methylbutin-3-ol, $\text{Me}_2\text{C}(\text{OH})\text{C}:\text{CH}$ (A). The A, which has thus far been described only in the patent literature (Farbenfabriken vorm. F. Bayer & Co., *Ger. pats.* 280,226, 285,770, 286,920, 288,271), is prepd. by the action of C_2H_2 on CH_3CMeONa (obtained from Me_2CO and NaNH_2 in Et_2O at a low temp.). The product so obtained is contaminated with mesityl oxide and the A is purified through the Ag salt. In the prepn. of A, $(\text{HOCMe}_2\text{C})_2$ (B) is also formed as a by-product. Passed in vapor form over MgSO_4 at 250° A loses 1 mol. H_2O and yields isopropenylacetylene (3-methyl-3-buten-1-ine), $\text{CH}_2:\text{CMeC}:\text{CH}$ (C). The metallic derivs. of C condense with acid chlorides to ketones (intense cooling must be provided for; otherwise there is much resinification). C itself reacts with Grignard reagents, RMgX , with evolution of RH and formation of the Mg deriv. of C, which then reacts in the usual way with aldehydes and ketones. In the presence of certain catalysts the triple bond in A can be made to take up 1 mol. H_2O . With HgSO_4 in an excess of dil. H_2SO_4 there is obtained almost quant. $\text{Me}_2\text{C}(\text{OH})\text{COMe}$ (D); with boiling dil. H_2SO_4 alone or with H_2SO_4 in AcOH C is first formed and then to a large extent resinifies. Shaken in petr. ether with P_2O_5 D yields an anhydride, $(\text{O.CMe}_2\text{CMe})_2\text{O}$ (E), of the tautomeric hemi-acetal form; dil. mineral acids reconvert

it into D; with Br it evolves HBr and yields a stable cryst. compound (F), probably $[\text{O.CMe}_2\text{C}(\text{CH}_2\text{Br})]_2\text{O}$. In the presence of alkalis, however, D has pronounced ketonic

properties, yielding a normal semicarbazone and oxime and condensing, by the Claisen method, with aromatic aldehydes to well crystd. compds., e. g., with BzH to 1-phenyl-4-methylpenten-4-ol-3-one (G), which give normal oximes and acetates; with $o\text{-H}_2\text{NC}_6\text{H}_4\text{CHO}$ ring formation and elimination of H_2O occur and the product is 2- α -hydroxyisopropylquinoline (H). A is a mobile liquid of peculiar odor, miscible with H_2O in all proportions, b. 103–4°, d_4^{20} 0.8651, n_D^{20} 1.41867, d_4^{15} 0.8678, n_D^{15} 1.41536 and 1.42446 for α and β at 15.8°, E_S –0.44, –0.35, –0.49, 2.2% for α , D, β and $\beta-\alpha$; acetate, b. 133–5°. C, mobile liquid of penetrating odor, b. 32–5°, is almost insol. in H_2O and easily sol. in all org. solvents, partly polymerizes and becomes yellow on standing, forms, even in traces, a characteristic lemon-yellow Cu' salt, d_4^{15} 0.6801, n_D^{15} 1.41666, n_D^{15} 1.43046, E_S 2.68, 2.88, 31.5% for α , β and $\beta-\alpha$. D b. 140–1°, $d_4^{17.2}$ 0.9578, $n_D^{17.2}$ 1.41425, $n_D^{17.2}$ 1.42203, E_S –0.04, –0.03, 2.3% for α , β and $\beta-\alpha$; semicarbazone, m. 164°; oxime, m. 86°; acetate, oil of peppermint-like odor, almost insol. in H_2O , easily sol. in the usual org. solvents, b. 171–2°, $d_4^{17.4}$ 1.0064, $n_D^{17.4}$ 1.41485, $n_D^{17.4}$ 1.42302, E_S –0.12, –0.09, 5.1% for α , β and $\beta-\alpha$. G (benzal methyl α -hydroxyisopropyl ketone), greenish yellow, extraordinarily refractive oil, b. 164–9°, m. 30–40°; oxime, m. 136°; acetate, m. 85°. 1-3',4'-Methylenedioxyphenyl-4-methylpenten-4-ol-3-one (piperonylidene methyl α -hydroxyisopropyl ketone), fine yellow leaflets from dil. alc., m. 105–6°, acetate, m. 93°. 1-Phenyl-6-methyl-

hepta-1,3-dien-6-ol-5-one (cinnamylidenemethyl α -hydroxyisopropyl ketone), light yellow leaflets from alc., m. 109–10°; *acetate*, m. 58–9°. *1- α -Furyl-4-methylpenten-4-ol-3-one (α -furfuralmethyl α -hydroxyisopropyl ketone)*, light yellow, strongly refractive, viscous oil, b. 140–5°, very quickly turns dark brown in the air; *acetate*, leaflets from dil. alc., m. 49°. *H* (*dimethyl-2-quinolylcarbinol*), cryst. powder from petr. ether, m. 64–5°, practically insol. in H₂O, easily sol. in HCl, repptd. by NaOH, sol. in excess of NH₄OH and repptd. on cautious neutralization. *E*, oil of camphor-like odor, insol. in H₂O, easily sol. in org. solvents, b. 165–7°, $d_4^{17.8}$ 0.9702, n_D 1.41696, n_D 1.42456, E_D –0.25, –0.21, 10% for α , β and β – α . *F*, cryst. powder from dil. alc., m. 64–5°, almost insol. in H₂O, easily sol. in the usual org. solvents. C. A. R.

Reactions of combination with conjugated systems of double linkings. I. Bromination of isoprene. A. G. BERGMANN. *J. Russ. Phys. Chem. Soc.* 52, 24–37 (1920).—Mols. composed of 2 similar atoms or groups of atoms unite with a conjugated system of double C linkings at the 1- and 4-positions, *i. e.*, at the ends of the system, an exception to this rule occurring in the combination of Br with aromatic derivs. As regards mols. consisting of dissimilar components, such as HBr, few expld. data are available, but the union does not take place in accordance with Thiele's law. Bromination of isoprene in CHCl₃ soln., cooled in ice yields: (1) A small quantity of the *monobromo compd.*, CH₂-BrCMe:C:CH₂(?), b_M 61.5–2.5°, d_{20} 1.3742. (2) The dibromide, C₅H₈Br₂, b_{10} 62–4°, d_{20} 1.7431, which gives the dibromoglycol, b. 126.5°, when oxidized by KMnO₄. (3) The isomeric dibromide, b_{10} 88–92°, d_{20} 1.7880. This dibromide yields a viscous, oily ozonide, which is decompd. by boiling water, giving bromoacetone, BrCH₂CO₂H, and a tarry mixt. of bromoaldehydes, bromoketones, peroxides, etc. Oxidation of the dibromide by means of KMnO₄ yields the dibromoglycol, which is sparingly sol. in water, while treatment with CrO₃ gives bromoacetone and BrCH₂CO₂H (cf. Mokiewsky, *J. Russ. Chem. Soc.* 30, 885–900 (1898); 32, 207–16 (1900); 36, 912 (1904)). With NH₃ the dibromide forms an amorphous, sometimes glue-like substance of high mol. wt., and with sodamide an amorphous, insol. product contg. 32.51–32.89% of Br and 7.87–7.93% of N. II. Combination of hydrogen bromide with di-isopropenyl [β , γ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene]. *Ibid* 37–40.—The combination of HBr with β , γ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene in glacial AcOH takes place in the 2 stages: (1) CH₂:CMeCMe:CH₂ + HBr = CMe₂BrCMe:CH₂, and (2) the latter + HBr = CMe₂BrCMe₂Br (30%) + CMe₂-BrCHMeCMe₂Br (70%). γ -Bromo- β , γ -dimethyl- Δ^{α} -butene, C₆H₁₀Br, b_{100} 84–6°, d_{20} 1.2201, yields dimethylisopropenylcarbinol when hydrolyzed by means of aq. KOH. β , γ -Dibromo- β , γ -dimethylbutane was described by Thiele (*Ber.* 27, 454). α , γ -Dibromo- β , γ -dimethylbutane is a liquid, $b_{16.5}$ 83–9°, d_{20} 1.6065. The product of the union of 1 mol. of HBr with isoprene, *viz.*, γ -bromo- γ -methyl- Δ^{α} -butene, combines with a 2nd mol. of HBr, apparently giving only β , δ -dibromo- β -methylbutane. J. C. S.

The use of paraformaldehyde (gaseous formaldehyde) and paraldehyde (gaseous acetaldehyde) in the synthesis of alcohols. C. E. WOOD AND FRANK SCARF. *J. Soc. Chem. Ind.* 42, 13–15T (1923).—*sec*-Butyl alcohol was prepd. in a 67% yield by passing gaseous AcH, obtained by depolymerization of paraldehyde with 5 *N* H₂SO₄, into a carefully prepd. Et₂O soln. of EtMgBr; after removal of the Et₂O the condensation product was stirred into an ice-cold soln. of NH₄Cl, from which the alc. was steam-distd. off, and subsequently fractionated. In a similar manner, 76% *sec*-amyl alcohol was obtained from PrMgBr and AcH, 67% *sec*-butylcarbinol from *sec*-BuMgBr and HCHO (prepd. by warming paraformaldehyde), and 53% *sec*-amylcarbinol from *sec*-C₄H₉MgBr and HCHO. T. S. CARSWELL

Role of phosphorus pentoxide in the splitting off of water from alcohol and ether. D. BALAREW. *J. prakt. Chem.* 104, 368–77 (1922).—Upon the gradual addn. of P₂O₅ to a mixt. of abs. EtOH and Et₂O, HPO₃ results, and slowly dissolves in the mixt., form-

ing EtH_2PO_4 . An intermediate product of the reaction is $\text{Et}_2\text{H}_2\text{P}_2\text{O}_7$. Upon long standing or upon heating, the amt. of $\text{Et}_2\text{H}_2\text{P}_2\text{O}_7$ decreases with the formation of EtH_2PO_4 . Other products of the reaction are neutral esters and perhaps other phosphates. Little if any EtPO_3 is formed. The formation of C_2H_4 depends upon the instability of these esters, and the catalytic action of P_2O_5 in the splitting off of H_2O from EtOH and Et_2O depends upon its capacity to unite with alkyl hydrates and oxides. C. J. WEST

Photocatalysis. III. The photosynthesis of naturally occurring nitrogen compounds from carbon dioxide and ammonia. E. C. C. BALY, I. M. HEILBRON AND H. J. STERN. *J. Chem. Soc.* 123, 185-97 (1923); cf. *C. A.* 16, 3463.—The 1st step in the action of light from the Hg quartz lamp is the formation of MeNH_2 , some HNO_2 and HNO_3 being formed at the same time. Continued action of the light leads to the formation of $\text{C}_2\text{H}_5\text{N}$ and $\text{C}_3\text{H}_7\text{N}$, which may be formed by the action of the activated HCHO on the MeNH_2 or by the direct action of 5 mols. HCHO and 1 mol. NH_3 . No compds. intermediate between MeNH_2 and $\text{C}_2\text{H}_5\text{N}$ have been found. Still further exposure leads to more complex alkaloidal compds. of which it is believed that coniine has been identified, both chem. and pharmacol. This is doubtless synthesized by the action of the activated HCHO upon $\text{C}_2\text{H}_5\text{N}$. After all the N-contg. compds. are removed from the reaction flask, no trace of sugar or NH_2 -acids is found. C. J. WEST

The β -chlorovinylchloroarsines. W. LEE LEWIS AND G. A. PERKINS. *Ind. Eng. Chem.* 15, 290-5 (1923).—A mixt. of AsCl_3 and AlCl_3 absorbs C_2H_2 readily at room temp., forming, among other probable addn. products, the compd. $\text{AlCl}_3 \cdot 3\text{C}_2\text{H}_2 \cdot \text{AsCl}_3$. On distn., 3 products are obtained: β -chlorovinylchloroarsine, $(\text{CHCl} : \text{CH})\text{AsCl}_2$, b_{780} 190°, d_{40} 1.888; bis- β -chlorovinylchloroarsine, $(\text{CHCl} : \text{CH})_2\text{AsCl}$, b_{780} 230°, d_{40} 1.702; and tris- β -chlorovinylarsine, b_{780} 260°, d_{40} 1.572. The vapors of the first 2 are strongly vesicant, while the 3rd is almost without action. When the crude reaction mixt. was distd., the residue in the flask exploded when it became coned.; this difficulty was avoided by flash distn., in which the liquid was slowly dropped into a flask held at 220° under 20-60 mm. The product from the flash distn. was then fractionated in a continuous still. On distn., $(\text{CHCl} : \text{CH})_2\text{As}$ and $(\text{CHCl} : \text{CH})_2\text{AsCl}$ were slowly converted into $\text{CHCl} : \text{CHAsCl}_2$. On long standing, the content of the primary compd. in the original mixt. was also increased. T. S. CARSWELL

Alcoholates of thallium. R. DE FORCRAND. *Compt. rend.* 176, 20-3 (1923).—In prep. derivs. of EtOH , AmOH , and MeOH of the constitution ROTi , Lamy (*Ann. chim. phys.* [3] 67, 395; [4] 3, 373) found that Tl does not react either with pure alcs. or pure H_2O ; derivs. are best made from thallium ethylate (A), which is first prepd. by exposing chips of Tl under a bell-jar to abs. EtOH vapor, while conducting in air or O to complete the reaction $2\text{EtOH} + \text{Tl}_2 + \text{O} \longrightarrow \text{H}_2\text{O} + 2\text{EtOTl}$. A, an oily liquid, d. 3.55, is the starting-material in the prepn. of the following compds.: thallium hydroxide, TiOH (B), by mixing A with 1 vol. (about 4 mols.) of cold H_2O , a beautiful yellow compd.; monothallium glycolate, $\text{HOC}_2\text{H}_4\text{OTl}$ (C), from a mixt. of 1 mol. each of glycol and A, a bright yellow ppt. with greenish cast, resembling $\text{UO}_2(\text{NO}_3)_2$; monothallium glycerolate, $\text{C}_3\text{H}_5(\text{OH})_2\text{OTl}$, a grayish solid compd. similar to C; these 3 compds. give colorless H_2O solns.; thallium phenolate, PhOTl (D), by mixing PhOH and A in cold dry Et_2O , a white microcryst. powder somewhat like MeOTl ; thallium acetate, by adding 1 mol. AcOH to A in dry Et_2O , resembles D; thallium sulfate, Tl_2SO_4 , by dissolving B in dil. H_2SO_4 . Certain samples of impure Tl are attacked by dil. H_2SO_4 ; contact with Pt accelerates the reaction; pure Tl is much less reactive in this respect than pure Zn, but B in H_2O combines with the weakest acids, even with alcs. A thermochem. study of the above compds. is being made. A. R. ALBRIGHT

Aluminium trialkyl etherates. ERICH KRAUSE AND BRUNO WENDT. *Ber.* 56B, 468-72 (1923).—"Elektron" metal (15.16% Al, 0.24% Si, and Mg) reacts readily with

EtBr in Et₂O, giving *aluminium triethyl etherate*, mobile liquid, b_{11} 112°, which analyzes for 4AlEt₃·3Et₂O. It b. 216–8° with very little decompn. or loss of Et₂O. In the air it fumes vigorously, while with H₂O it explodes violently. It was also obtained by treating pure AlEt₃ with Et₂O and from EtMgBr and anhyd. AlCl₃. Other phys. consts. are: $b_{11.4}$ 110.5°, $d_{17.4}^{17.4}$ (vacuum) 0.8200, $n_{D,20}$ 1.43433, n_D 1.43700, $n_{H,20}$ 1.44349, $n_{H,17}$ 1.44884 at 17.4°. *Aluminium trimethyl etherate*, b_{11} 68°. *Aluminium tripropyl etherate*, b_{11} 135°.

C. J. WEST

Quantitative study of the reaction between ethylenic hydrocarbons and the Grignard reagent. HENRY GILMAN AND H. MARJORIE CRAWFORD. *J. Am. Chem. Soc.* **45**, 554–8 (1923).—Using the gas analysis method (C. A. 17, 530) to det. the amt. of the Grignard reagent (EtMgI) before and after treatment with various unsatd. hydrocarbons (ethylene, amylene, diallyl, cyclohexene, cyclohexadiene, phellandrene 1,1-diphenylethylene, -propylene and -amylene, 1,4-diphenylbutadiene and tetraphenylethylene), it was found that they do not add EtMgI, not only under ordinary conditions with 1 equiv. EtMgI in Et₂O but also in 1 expt. in which Ph₃C:CH₂ was refluxed 35 hrs. with 6 equivs. EtMgI and in another where (PhCH:CH)₂ was refluxed with EtMgI in boiling Bu₂O.

C. A. R.

The decomposition of formic acid by sulfuric acid. E. R. SCHIERZ. *J. Am. Chem. Soc.* **45**, 447–55 (1923).—The velocity of decompn. of HCO₂H by H₂SO₄ of 7 concns. (98.9% to 95%) at 10° intervals between 15° and 45° has been detd. by measuring the CO evolved. The reaction is of the 1st order and is probably a dehydration: $n\text{HCO}_2\text{H} + m\text{H}_2\text{SO}_4 \rightarrow n\text{CO} + m\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ (the H₂SO₄ is present in such large excess that its concn. is not appreciably altered during the reaction). Cu, Ag, K, Na or Hg' sulfates added to the H₂SO₄ retard the reaction only slightly. Me₂CO and AcOH act as inert diluents. HCl markedly increases the velocity of the reaction, probably acting as a catalyst. The temp. coeffs. of the reaction decrease regularly with increasing temps. except with 91.8% H₂SO₄, which shows some irregularities.

C. A. R.

The catalytic decomposition of formic acid in acetic anhydride. ERNEST R. SCHIERZ. *J. Am. Chem. Soc.* **45**, 455–68 (1923).—H₂SO₄, HNO₃, HCl, HF, H₃PO₄ and (CO₂H)₂ cause a catalytic decompn. of HCO₂H in Ac₂O; owing to side reactions between the catalyst and Ac₂O, no quant. detns. were possible. Tertiary N bases also cause a catalytic decompn. of HCO₂H in Ac₂O; the velocity of decompn. corresponds in a general way to the basicity of the N compd., very weak bases, such as caffeine, producing no decompn. The decompn. with C₆H₅N proceeds with different velocities in the solvents C₆H₆, PhMe, Me₂CO, CCl₄, PhNO₂, EtOH, AmOH, iso-BuOH, AmOAc and BzH. The velocity of the decompn. by brucine, strychnine, pyridine, quinine, morphine, nicotine, cocaine and papaverine at 50° was detd. quant. The reaction is of the 1st order and its velocity increases with increasing concn. of the catalyst; for C₆H₅N the function is linear, for the other bases, approx. linear. AcOH has an inhibitory effect on the catalysis by brucine, strychnine and morphine but not on that by C₆H₅N. This inhibitory action may be used as a quant. method for detg. AcOH in Ac₂O. The joint effect of quinine and brucine and of cocaine and brucine is equal to the sum of the separate effects of each catalyst. It is suggested that the reaction may proceed through an intermediate compd. of the mixed acetic-formic anhydride with the base: $\text{MeC}(\text{O})\text{O}(\text{N}:\text{R})\text{C}(\text{O})\text{H} + \text{N}:\text{R} \rightarrow \text{MeC}(\text{O})\text{O}(\text{N}:\text{R})\text{C}(\text{O})\text{H} \rightarrow \text{AcOH} + \text{N}:\text{R} + \text{CO}$.

C. A. R.

Dependence of rotatory power on chemical constitution. XIII. The spatial configuration of the unbranched aliphatic chain. R. H. PICKARD, JOSEPH KENYON AND HAROLD HUNTER. *J. Chem. Soc.* **123**, 1–14 (1923); cf. C. A. 9, 1036.—In a homologous series of optically active alcs. of the general formula RCH(OH)R', where R represents the growing aliphatic chain, departures from what may be termed the normal alteration of rotatory power with increase of mol. wt. are observed when R consists of

a chain of 5 or 10(11) C atoms. A similar phenomenon is observed in homologous series of esters of the formula $R'R''CHOCOR$ when the growing chain R contains 5 or 10(11) C atoms. This case differs from the 1st in that R is not directly attached to the asym. C atom. Alcs. of simple chem. constitution possess simple rotatory dispersive powers under widely varying conditions of temp., whereas the aliphatic esters derived from them show simple rotatory dispersive powers only at low temps.; at higher temps. and in soln. the dispersive powers become complex. *d-β-Butyl formate*, by heating the alc. with HCO_2H and $ZnCl_2$ on the H_2O bath for 0.5 hr., pleasant smelling liquid, b. $96-7^\circ$, $d_4^{21.5}$ 0.8820, d_4^{25} 0.8580, d_4^{30} 0.8364, d_4^{35} 0.8007, $n_{D,20}$ 1.3786, $n_{D,25}$ 1.3812, $n_{D,30}$ 1.3817, $n_{D,35}$ 1.3828, $n_{D,40}$ 1.3896 at 25.3° . *d-β-Octyl formate*, fragrant, limpid liquid, b_{70} $81-2^\circ$, $d_4^{12.5}$ 0.8718, d_4^{15} 0.8397, $d_4^{17.5}$ 0.8196, d_4^{20} 0.7954, $d_4^{22.5}$ 0.7591, $n_{D,20}$ 1.4174 at 12.5° . *d-γ-Nonyl formate*, limpid liquid, b_{12} $94.5-5^\circ$, d_4^{20} 0.8688, d_4^{25} 0.8509, d_4^{30} 0.8390, d_4^{35} 0.8153, d_4^{40} 0.7941, d_4^{45} 0.7778, d_4^{50} 0.7536, $n_{D,20}$ 1.4152, $n_{D,25}$ 1.4182, $n_{D,30}$ 1.4178, $n_{D,35}$ 1.4196, $n_{D,40}$ 1.4271, at 25.6° . *d-Benzylmethylcarbinyl formate*, mobile, highly refractive, penetrating liquid, b_{19} $108-10^\circ$, d_4^{25} 1.027, d_4^{30} 1.008, d_4^{35} 0.9800, d_4^{40} 0.9572, d_4^{45} 0.9324, d_4^{50} 0.9099, $n_{D,20}$ 1.4930, $n_{D,25}$ 1.4795, $n_{D,30}$ 1.4682, $n_{D,35}$ 1.5009, $n_{D,40}$ 1.5251 at 24.5° . Measurements of the rotatory power of the pure esters and of solns. in CS_2 , EtOH, C_6H_6 and Me_2CO at different temps. and with light of different wave lengths are reported. XIV. Normal aliphatic ethers of *d-β-octanol*. JOSEPH KENYON and R. A. McNICOL. *Ibid* 14-22.—Because the above results may be due to the sp. property of the CO_2H portion of the mol., an investigation was carried out on a series of ethers. At all temps. between 15° and 130° these compds. exhibit simple rotatory dispersion. The rotatory powers show the presence of marked depressions in the case of the members contg. the Pr, Am, C_6H_5 and C_6H_{17} group. The magnitude of the rotatory power may be influenced by the approx. closing of the spiral arrangement of 3 types of chain present in all these compds.: any complete chain through the mol.; the chain of atoms up to and including the asym. C atom; and the chain of atoms attached to the asym. C atom. In the case of the solns., CS_2 causes enhanced and EtOH depressed rotations, the reverse of all previous cases. The following ethers of *d-β-octanol* are reported: *Methyl*, b_{14} $76-7^\circ$, d_4^{20} 0.8094, n_D^{25} 1.4212; *ethyl*, b_{14} $63-5^\circ$, d_4^{20} 0.7861, n_D^{25} 1.4136; *propyl*, b_{14} 76° , d_4^{20} 0.7887, n_D^{25} 1.4148; *butyl*, b_{14} $85-6^\circ$, d_4^{20} 0.7923, n_D^{25} 1.4168; *amyl*, b_{14} 99° , d_4^{20} 0.7958, n_D^{25} 1.4218; *hexyl*, b_{14} 115° , d_4^{20} 0.7983, n_D^{25} 1.4252; *heptyl*, b_{14} 129° , d_4^{20} 0.8017, n_D^{25} 1.4267; *octyl*, b_{14} 140° , d_4^{20} 0.8038, n_D^{25} 1.4301; *nonyl*, b_{14} 163° , d_4^{20} 0.8042, n_D^{25} 1.4325. Density and optical rotations are given at several temps. and in the latter case for light of several wave lengths as well as in solns. of CS_2 and EtOH. XV. *n-Alkyl ethers of d-benzylmethylcarbinol*. HENRY PHILLIPS. *Ibid* 22-31.—Examn. of the ethers of *d-benzylmethylcarbinol* showed that they exhibit simple rotatory dispersion over the temp. range $20-140^\circ$ and further support is afforded to the view that complex rotatory dispersion must be regarded as a property of the CO_2H group as a whole and not of any one atom in it. The following ethers were prepd.: *Methyl*, b_{12} 85° , d_4^{25} 0.9314; *ethyl*, b_{12} 93° , d_4^{25} 0.9162; *propyl*, b_{12} 103° , d_4^{25} 0.9093; *butyl*, b_{12} 115° , d_4^{25} 0.8991; *amyl*, b_{12} 127° , d_4^{25} 0.8900; *hexyl*, b_{12} 137° , d_4^{25} 0.8878; *heptyl*, b_{12} 156° , d_4^{25} 0.8828; *octyl*, b_{12} 170° , d_4^{25} 0.8815; *nonyl*, b_{12} 170° , d_4^{25} 0.8820. n is given at 25° for $\lambda = 6438, 5896, 5461, 5086, 4800, 4678$ and 4358 . The density is given at several temps. and the optical rotations at several temps. and the above values for λ . Values for solns. in CS_2 and EtOH are also reported. XVI. The di-*d-β-octyl* esters of the saturated dicarboxylic acids. LESLIE HALL. *Ibid* 32-44.—All the esters described in this work exhibit complex rotatory dispersion under all conditions employed (in homogeneous condition at temps. from 20° to 130° and in soln. in CS_2 and EtOH at the ordinary temp.). The $(CO_2H)_2$ esters possess a particularly large optical rotation; the $(H_2CCO_2H)_2$ ester has a very small rotation. The rotation values are alternately high

and low as the series is ascended. This may be due to the alternate members of the $(\text{CO}_2\text{H})_2$ series possessing a *cis*- or *trans*-configuration, resp. The following compds. were studied: *d*- β -Octyl oxalate, b_{11} 198-9°; *malonate*, b_{15} 158-60; *succinate*, b_{16} 208-11°; *glutarate*, b_3 175-7°; *adipate*, b_2 175°; *pimelate*, b_3 188-90°; *suberate*, b_3 202-4°; *azelate*, b_2 208-10°; *sebacate*, b_7 240-2°; *nonanedicarboxylate*, b_1 205-7°; *decanedicarboxylate*, b_1 205-10°; *undecanedicarboxylate*, b_2 215-7°; *d*- β -octyl ethyl oxalate, b_{20} 138-40°; *malonate*, b_{15} 198-200°; *succinate*, b_{16} 160-2°; *d*- β -octyl methyl oxalate, b_{20} 130-2°; *succinate*, b_{15} 163-4°. *Densities* of these esters are reported at several temps. and *rotations* at several temps. and for several wave lengths, and also in solns. of EtOH and CS_2 . **XVII. A new type of Walden inversion.** HENRY PHILLIPS. *Ibid* 44-59.—*d*-Benzylmethylcarbinyl *p*-toluenesulfonate (A), formed by the interaction of the components in $\text{C}_6\text{H}_5\text{N}$, m. 94°; solns. in EtOH, C_6H_6 , CHCl_3 , CS_2 and $\text{C}_2\text{H}_5\text{N}$ are all *d*-rotatory (values given for $\lambda = 5893$, 5461, 4358). With EtONa in C_6H_6 or better heated under a reflux in abs. EtOH with K_2CO_3 , it forms $\text{Me}(\text{PhCH}_2)\text{CHOEt}$, b_{29} 92-4°, d_{25}^{25} 0.9177, n_D^{25} 1.4878, $[\alpha]_{5461}^{25}$ -19.9°. If, however, $\text{Me}(\text{PhCH}_2)\text{CHOK}$ reacts with $\text{EtOSO}_2\text{C}_6\text{H}_5$, the resulting ether has a *d*-rotation, $[\alpha]_{5461}^{25}$ 19.84°. Reaction of A with AcOK gave *l*-benzylmethylcarbinyl acetate, b_{18} 112-4°, d_{25}^{25} 0.9978, n_D^{25} 1.4881, $[\alpha]_{5461}^{25}$ -7.06°. A 2nd product of the reaction is the Et ether, which possessed $[\alpha]_{5461}^{25}$ -21.92°. In order to confirm the above reactions, the *l*-sulfonate (α_{5461} -6.92°) was treated with AcOK in EtOH; the resulting *d*-acetate showed α_{5461} 2.0. The same product was obtained in AcOH soln. Because of the difficulty of sepu. of the ether and acetate, the *l*-sulfonate was caused to react with BuCO_2K , giving the *d*-valerate, $\alpha_{5461}^{16.5}$ 9.76. From this it is seen that when the *d*-sulfonate reacts with EtOH in the presence of K_2CO_3 , there is a definite change in configuration (the *l*-ether results) in 1 stage; this is a definitely "abnormal" reaction. The same is true of the formation of the acetate and valerate. The fact that the reaction of the *l*-sulfonate and PhOK gave a product of the same sign as that between $\text{Me}(\text{PhCH}_2)\text{CHOK}$ and $\text{PhOSO}_2\text{C}_6\text{H}_5$ gives considerable support to the view of the mode of reaction put forward by Fergus and Lapworth (C. A. 6, 1742). **XVIII. The di-*l*-menthyl esters of the saturated dicarboxylic acids.** LESLIE HALL. *Ibid* 105-13.—The abnormal values of the rotatory power found by Hilditch (C. A. 4, 748) have no real existence; within the limits of exptl. error, the series shows a regular variation of rotatory power from member to member, except in the case of the oxalate and malonate and possibly with slight irregularities in the cases of the esters of the acids contg. 5 and 9 CH_2 groups. All esters exhibit simple rotatory dispersion under all the exptl. conditions studied. The sp. rotatory powers of these esters are influenced only slightly by change in temp. The following esters were studied: *di-l*-methyl malonate, b_1 169-70°, m. 61-2°; *succinate*, b_2 200-5°, m. 63°; *glutarate*, m. 45-6°, b_1 180-3°; *adipate*, b_1 190-4°, m. 63-4°; *pimelate*, b_2 216-7°, m. 45°; *suberate*, b_1 205-8°, m. 36-7°; *azelate*, b_2 225-8°; *sebacate*, b_1 216-7°; *nonane- α,ω -dicarboxylate*, b_2 235-8°; *decane- α,ω -dicarboxylate*, b_2 225-8°. Observations on *density* and *rotatory power* are given for several temps. and for different wave lengths, and *rotations* are given for an approx. 5% soln. in CHCl_3 . C. J. WEST

Products of polymerization of hydrocyanic acid. E. GRISZKIEWICZ-TRUCHIMOWSKI. *Roczniki Chemii* 1, 468-78 (1921).—The constitution $\text{NH}_2\text{CH}(\text{CN})_2$ has been suggested for the trimeride of HCN. In order to verify the presence of the NH_2 group, 2 reactions were investigated, *viz.*, condensation with aldehydes and the action of HNO_2 . The 1st reaction followed the course expected, and the following compds. were obtained. With salicylaldehyde, the *salicylidene deriv.*, $\text{CH}(\text{CN})_2\text{N}:\text{CHC}_6\text{H}_4\text{OH}$, yellowish green needles, m. about 235° (decompn.). With anisaldehyde, the *anisylidene deriv.* With BzH , the *benzylidene deriv.*, brown plates, m. 190° (decompn.). A *benzoyl deriv.* of the trimeride was also prepd., brown plates, m. 220° (decompn.), together with its unstable

hydrochloride. The results with HNO_2 were not those expected; it was thought that a diazo compd. would be formed, from which tartaric acid could be obtained by the following reaction: $\text{CH}(\text{CN})_2\text{NH}_2 \longrightarrow \text{CH}(\text{CN})_2\text{N}:\text{NOH} \longrightarrow (\text{CN})_2\text{CHOH} \longrightarrow [\text{CH}(\text{OH})\text{CO}_2\text{H}]_2$. The product of the reaction does not, however, decomp. on boiling; it is obtained from the solu. in orange prisms, m. about 145° , and is shown to be *4,5-dicyano-1,2,3-triazole*. On sublimation at 140° , this is obtained in a colorless modification, for which the constitution $\text{NH}_2\text{N}:\text{C}(\text{CN})\text{C}(\text{CN})\text{N}$ is suggested. The Ag, Cu, Ba,

K, and NH_4 salts of the dicyanotriazole were prepd., also its *1-methyl deriv.*, m. $57.5-8.5^\circ$. Hydrolysis with HCl gives the *4-amide* of 1,2,3-triazole-4,5-dicarboxylic acid, m. 275° . By passing HCl through the substance in Et_2O is obtained *ethyl 4-cyano-1,2,3-triazole-5-carboxylate*, m. $114-5^\circ$ from which the *acid*, m. $225-6^\circ$, is obtained, and from this by hydrolysis with H_2SO_4 the 4,5-di- CO_2H acid, m. $195-6^\circ$, is produced. It is suggested that the dicyanotriazole may be produced from the HNO_2 by condensation of a diazotized mol. of it with an undiazotized one. The results both with aldehydes and with HNO_2 , therefore, support the view that the trimeride of HCN is $\text{CH}(\text{CN})_2\text{NH}_2$.

J. C. S.

The photochemically sensitive compounds of molybdc and formic acids. W. F. JAKÓB. *Rozniki Chemji* 1, 411-23(1921).—The salts of molybdeno-orthoformic acids are prepd. and investigated. From six possible types of acids, J. succeeds in prep.

only the Na, K, and NH_4 salts of the types: $\left[\text{CH} \begin{smallmatrix} \text{Mo}_2\text{O}_7 \\ (\text{OH})_2 \end{smallmatrix} \right]_X$, and $\left[\text{CH} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \begin{smallmatrix} \text{Mo}_2\text{O}_7 \\ \text{O} \end{smallmatrix} \right]_X$, and a salt, probably $\left[\begin{smallmatrix} \text{Mo}_2\text{O}_7 & \text{H} & \text{H} & \text{Mo}_2\text{O}_7 \\ & \text{C} & & \text{C} \\ & \text{O} & \text{Mo}_2\text{O}_7 & \text{O} \end{smallmatrix} \right] \text{K}_4\text{H}_2\text{O}$. All the salts prepd. are

photochem. sensitive, becoming green, yellow, or brown on exposure to light. They are obtained as cryst. ppts. from solns. of the respective molybdates, strongly acidified with HCO_2H . They cannot be recrystd., as they decomp. in soln.

J. C. S.

The action of polyhalogenated compounds of methane and of ethane on magnesium derivatives. II. R. BINAGHI. *Gazz. chim. ital.* 52, II 132-8(1922).—Recently Oddo and B. (C. A. 16, 1392) found that PhMgBr acting on CHI_3 gave $\text{BrMgC}:\text{CMgBr}$, I_2CHMgBr , $\text{ICH}(\text{MgBr})_2$ and $(\text{Ph}_2\text{CH})_2$ (A) instead of CHPh (B). Before passing to other polyhalogen derivs. of CH_4 and C_2H_6 B. studied the action of CHCl_3 and CHBr_3 on PhMgBr and EtMgBr , resp. The activity with PhMgBr decreases in the order CHI_3 , CHBr_3 , CHCl_3 . With CHI_3 no B is obtained, while with CHCl_3 B is the sole product obtained. With CHBr_3 A is formed but B is the main product. The 1st step in the reaction may be represented thus: $2\text{PhMgX} + \text{X}_2\text{CX} \longrightarrow 2\text{MgX}_2 + \text{Ph}_2\text{CHX}$; and then both (a) $\text{Ph}_2\text{CHBr} + \text{PhMgBr} \longrightarrow \text{MgBr}_2 + \text{CHPh}$; and (b) $2\text{Ph}_2\text{CHBr} + \text{PhMgBr} \longrightarrow \text{MgBr}_2 + \text{PhBr} + (\text{Ph}_2\text{CH})_2$ take place in the case of CHBr_3 . CHBr_3 acts on EtMgBr like CHI_3 , giving C_2H_5 , C_2H_6 , CH_4 , EtBr and CH_2Br_2 as well as a little CH_2Et . The reactions are represented thus: $3\text{EtMgBr} + 2\text{CHBr}_3 \longrightarrow 3\text{MgBr}_2 + 3\text{EtBr} + \text{C}_2\text{H}_6$ and then $\text{C}_2\text{H}_6 + 2\text{EtMgBr} \longrightarrow 2\text{C}_2\text{H}_5 + \text{BrMgC}:\text{CMgBr}$ and $\text{BrMgC}:\text{CMgBr} + 2\text{H}_2\text{O} \longrightarrow 2\text{MgBrOH} + \text{C}_2\text{H}_2$. With H_2O the reaction mass also gave CH_2Br_2 , CH_3Br and CH_4 . With CHCl_3 + EtMgBr only a trace of C_2H_4 was formed and the gas was C_2H_4 + C_2H_6 . CH_2Et and a little $\text{C}_2\text{H}_5\text{Br}_2$ were formed. The reaction mass gave no gas on treatment with H_2O , which B. cannot interpret fully. For details of manipulation and sepn. of products see the original.

E. J. WITZEMANN

The complex salt of mercuric acetate and sulfide. A. MIOLATI. *Gazz. chim. ital.* 52, II, 27(1922).—Recently Bernardi and Rossi (C. A. 16, 2113) reported a complex $\text{HgS.Hg}(\text{OAc})_2$ which was previously obtained by Palm (1862) and which is listed in Beilstein and Gmelin-Kraut. HgS gives with other Hg salts such as HgCl_2 and HgI_2

compds. having a complex cation of which the HgS forms a part (Borelli, *C. A.* **5**, 1717).

E. J. WITZERMANN

Velocity of hydrolysis of acetic anhydride. ANTON SKRABAL. *Monatsh.* **43**, 493-506(1923).—The velocity of the hydrolysis of Ac_2O in H_2O has been measured by combining the reaction with a 2nd reaction, $\text{KI} + \text{KIO}_3$. A relation is developed between the velocity consts. of the 2 equations and the elec. dissociation const. of AcOH so that the rate of hydrolysis of Ac_2O can be calcd. from the known rate of the formation of I . The value found for k_w (0.19) agrees with previously detd. values. The const. of the alk. sapon of Ac_2O , k_a , was found to be $\leq 4.4 \times 10^{-6}$ as the upper limit. The velocity of the aq. sapon. is retarded by AcMc . This is a medium action.

C. J. WEST

Dynamics of the formation of nitriles from acid anhydrides and amides. II. The kinetic study of the reaction between acetamide and acetic anhydride, using phase rule methods. ROBERT KREMANN, ALFRED ZOFF AND VIKTOR OSWALD. *Monatsh.* **43**, 139-44(1922); cf. *C. A.* **12**, 2194.—The reaction $\text{AcNH}_2 + \text{Ac}_2\text{O} = \text{MeCN} + 2\text{AcOH}$ is followed kinetically, the method consisting in taking the f. ps. of mixts. of the components which had been heated at the required temp. for different lengths of time. The % compns. were then read off from an exptly. detd. curve of the f. ps. of mixts. of the 2 systems involved in the reversible reaction. The above reaction reaches an equil. corresponding to 83% conversion (from left to right in the sense of the above scheme) at 98° and with 87% conversion at 78° . **III.** Reaction between benzamide and acetic anhydride. R. KREMANN, WILHELM RÖSLER AND WILHELM PENKNER. *Ibid* 145-59.—When equimol. amts. of Ac_2O and BzNH_2 are heated together BzNHAc is formed in addn. to PhCN and AcOH . In studying the reaction, therefore, a ternary f. p. diagram was constructed for the systems BzNH_2 and Ac_2O , PhCN and 2AcOH , and BzNHAc and AcOH . Using this diagram, the progress of the reactions was followed by a series of f. p. detns. The values detd. for the compn. of the equil. mixt. were: BzNH_2 , 0.48 mol.; Ac_2O , 0.48; BzNHAc , 0.38; AcOH , 0.66; PhCN , 0.14. **IV.** The reaction between acetamide and benzoic anhydride. R. KREMANN, ALOIS AUER, VIKTOR OSWALD AND ALFRED ZOFF. *Ibid* 345-58(1923).—The behavior of mixts. of AcNH_2 , Bz_2O , MeCN , BzOH and AcNHbz was studied as regards the temp. of primary crystn. from the molten mass and the results are reported in tables and curves. The fact that MeCN formation from AcNH_2 and Bz_2O proceeds only to the extent of about 0.69 mol. is explained by the formation of an equimol. addn. compd. **V.** The kinetic study of the reaction $1 \text{ benzoic anhydride} + 2 \text{ acetic acid} \rightleftharpoons 2 \text{ benzoic acid} + 1 \text{ acetic anhydride}$. R. KREMANN AND WILHELM RÖSLER. *Ibid* 358-65.—The equil. const. is calcd. to be 6.4, which indicated that Bz_2O is a stronger agent than Ac_2O in the production of anhydrides. The effect of the formation of a mixed anhydride is discussed.

C. J. WEST

The action of organomagnesium compounds on nitriles. FRANZ BAERTS. *Bull. soc. chim. Belg.* **31**, 184-92(1922).—A study of the action of Grignard's reagent on EtCN to det. whether the latter yields condensation products similar to those obtained from MeCN (cf. Bruylants, *Bull. acad. Belg.*) and also ketones according to Blaise's reaction (*Compt. rend.* **132**, 38-41(1901)). With EtMgBr , after treatment with water, 2 substances are obtained from the nitrile, termol. cyanoethane, $(\text{EtCN})_2$, and Et_4CO , the latter in much larger proportion. In addn., a considerable quantity of Et_4COH and bimol. cyanoethane, $(\text{EtCN})_2$, is formed in the reaction. The bimol. polymeride, which is the major product in the case of MeCN , is in this case about 25% of the total. The formation of the polymerides is explained on the hypothesis that the nitrile acts as a pseudo-acid and schemes are suggested to account for the formation of these and other products.

J. C. S.

Butenonitriles. P. BRUYLANTS. *Bull. soc. chim. Belg.* 31, 175-84(1922).—The prepn. of β -butenitrile (vinylacetonitrile) from allyl iodide and CuCN (Henry, C. A. 10, 1506) need not be carried out under pressure; the reaction takes place with equal ease in the case of allyl bromide, and, in addn., the yield is quant. The following phys. consts. are given: $b_{710.4}$ 118.4-8.6°, m. (after solidification in liquid air) 84°, n_{D}^{20} 1.40297, n_{D}^{20} 1.40602, $n_{H\beta}^{20}$ 1.41170, d_4^{20} 0.83409. An isomeric may be obtained by gently heating γ -chlorobutyronitrile and also from the corresponding Br compd. Decompn. into the unsatd. nitrile and the halogen acid takes place, but in the latter case β -bromobutyronitrile is formed simultaneously. This isomeride, crotononitrile, may also be obtained from vinylacetonitrile by addn. of gaseous HCl or HBr and subsequent treatment with KOH or pyridine. It consists of a mixt. of the 2 possible stereoisomerides, which can only be sepd. after repeated fractionation. Phys. consts. have been detd. as follows: fraction b. 107.6-7.6°, $n_{H\alpha}^{20}$ 1.41503, n_{D}^{20} 1.41821, $n_{H\beta}^{20}$ 1.42650, d_4 0.8244; fraction b. 120.3-0.5°, $n_{H\alpha}^{20}$ 1.41835, n_{D}^{20} 1.42161, $n_{H\beta}^{20}$ 1.42985, d_4^{20} 0.8239, and it is on the evidence afforded by these that B. bases his views as to the space configuration of the substances, as chem. methods of investigation have not, as yet, given any trustworthy indication. II. *Ibid* 225-30.—Vinylacetonitrile reacts readily with alcs., yielding β -alkoxybutyronitriles, when a trace of the corresponding Na alkoxide is present. In the case of the lower alcs., the yield is diminished by reason of the polymerization of the nitrile. The additive products, of the general formula ROCHMcCH₂CN, are liquids of pleasant odor; the following have been prepd.: β -methoxybutyronitrile, b_{713} 169-70°, d_{20} 0.91643, $n_{H\alpha}^{20}$ 1.40664, n_{D}^{20} 1.40938, $n_{H\beta}^{20}$ 1.41363; β -ethoxybutyronitrile $b_{714.7}$ 175.5-6.5°, d_{20} 0.89164, $n_{H\alpha}^{20}$ 1.40814, n_{D}^{20} 1.41076, $n_{H\beta}^{20}$ 1.41537; β -propoxybutyronitrile, $b_{714.4}$ 192-3°, d_{20} 0.88312, $n_{H\alpha}^{20}$ 1.41183, n_{D}^{20} 1.41443, $n_{H\beta}^{20}$ 1.41908; β -isopropoxybutyronitrile, $b_{714.2}$ 182-3°, d_{20} 0.87408, $n_{H\alpha}^{20}$ 1.40994, n_{D}^{20} 1.41235, $n_{H\beta}^{20}$ 1.41759; β -allyloxybutyronitrile, b_{718} 196-8°, d_{20} 0.90165, $n_{H\alpha}^{20}$ 1.42178, n_{D}^{20} 1.42441, $n_{H\beta}^{20}$ 1.42935; β -butoxybutyronitrile, $b_{717.4}$ 209.5-10.5°, d_{20} 0.87785, $n_{H\alpha}^{20}$ 1.41765, n_{D}^{20} 1.41961, $n_{H\beta}^{20}$ 1.42474; β -isobutoxybutyronitrile, $b_{720.4}$ 201-201.5°, d_{20} 0.86876, $n_{H\alpha}^{20}$ 1.43123, n_{D}^{20} 1.41573, $n_{H\beta}^{20}$ 1.42073. An attempt to prep. the phenol deriv. was not successful, leading to the formation of a mixt. of the two crotononitriles from the vinylacetonitrile; B. states that this is due to the formation of an additive product and its subsequent decompn. The action of concd. H₂SO₄ on the nitrile results in the formation of isocrotonic acid, and the mechanism of the reaction is discussed. J. C. S.

Formation of hydroxamic acids from ketene. C. DEW. HURD AND P. B. COCHRAN. *J. Am. Chem. Soc.* 45, 515-21(1923); cf. C. A. 16, 415.—As was expected, CH₂:CO with free NH₂OH gives AcNHOH. With hydroxamic acids, RCONHOH, in AcOEt it also reacts normally like other acylating agents, adding to the α -H atom and yielding dihydroxamic acids, RCONHOAc, in excellent yield; when an excess of CH₂:CO is used trihydroxamic acids, RCONAcOAc, are obtained almost quant. An app. is described whereby the CH₂:CO can be obtained in 17.5% yield, based on the amt. of Me₂CO not recovered, by a modification of Schmidlin and Bergman's method (decompn. of Me₂CO at 600°). *Diacetylpyromucylhydroxamic acid*, (C₆H₅O)CONAcOAc, m. 54-5°. C. A. R.

Ethylene glycol: its uses and properties. G. O. CURME, JR. AND C. O. YOUNG. *Chem. Met. Eng.* 28, 169-70(1923).—C₂H₄(OH)₂ is a water-white liquid, d. 1.116, b_{710} 198°, and is hygroscopic in the air. It may find tech. application as a solvent, a preservative, or an org. chemical. T. S. CARSWELL.

Action of sulfuric acid upon higher diprimary glycols. ANOLF FRANK and OTTO LIEBERMANN. *Monatsh.* 43, 589-99(1923); cf. C. A. 9, 910.—The action of 75 g. concd. H₂SO₄ upon 6.5 g. HOCH₂(CH₂)₃CH₂OH gave 1,5-oxidononane, PrCH(CH₂)CH₂O,

b. 175-7°, the structure of which was established by oxidation with KMnO_4 to $n\text{-C}_{18}\text{H}_{36}\text{O}_2$ and $(\text{CH}_2\text{CO}_2\text{H})_2$, together with small amts. of $(\text{CO}_2\text{H})_2$ and AcOH . *Octadecanedioic*, $(\text{CH}_2)_{16}(\text{CH}_2\text{OH})_2$, m. 92°, was prepd. by the reduction of the corresponding ester by Na in EtOH. Its constitution was established by oxidation to the acid. The action of H_2SO_4 gave *1,5-oxido-octadecane*, which, because of the very small yield, was not characterized; for the same reason the results of the oxidation were not definite.

C. J. WEST

Dioximes. III. G. PONZIO. *Gazz. chim. ital.* 52, II, 145-60(1922).—See C. A. 17, 87.

E. J. WITZEMANN

Hydrolysis of lactic acid lactide. OTTO RINGER AND ANTON SKRAHAL. *Monatsh.* 43, 507-23(1923).—The hydrolysis of $\text{MeCH}_2\text{O.CO.CHMe}_2\text{O.CO}$ takes place in 2 steps:

$\text{MeCH}(\text{CO}_2\text{H})\text{OCOCH}(\text{OH})\text{Me}$ and $2\text{MeCH}(\text{OH})\text{CO}_2\text{H}$. The following values were found for alk., acid and aq. hydrolysis: 1st step: 1,200,000, 0.1088, 0.00459; 2nd step: 19.5, 0.00203. — The elec. dissociation const. of lactic acid is 9.9×10^{-4} at room temp.

C. J. WEST

Thionylidiacetic acid. KARL JÖNSSON. *Svensk Kem. Tids.* 34, 192-6(1923).—Thionylidiacetic acid has been prepd. by oxidizing thiodiglycolic acid with H_2O_2 . This is best done in acetone with a 25% excess of the H_2O_2 . It has been previously prepd. by Gazdar and Smiles (C. A. 3, 886; 5, 1082) who stated that their prepn. was "obviously pure" (m. 80°). The pure compd. m. 119°, is very sol. in water, slightly sol. in acetone, alc. and glacial AcOH , but very much less sol. in Et_2O and similar solvents. The aq. solus. heated or acidified decomp. into glyoxylic and thioglycolic acids. Its dissociation const. is 6.68×10^{-3} at 18°, 4.8×10^{-3} at 25°; (thiodiglycolic acid at 25°, 4.8×10^{-3} sulfonidylidiacetic acid, 25°, 1.3×10^{-2}). The salts are more stable than the acids. The Ba salt crystals with 1.5 H_2O (not $2\text{H}_2\text{O}$; cf. G. and S.). When the acid is heated to its m. p. there is a rapid rise in temp. with evolution of vapor. If care is taken to keep it just at the m. p. for some time there is no such vapor and crystals form in the melt. Glyoxylic acid and a tribasic acid, m. 158°, were identified in this mass. If the acid is heated just to a clear melt and then placed in the vacuum desiccator a product is formed in which may be identified; glyoxylic and thioglycolic acids and a lactone $\text{HO}_2\text{CCH}_2\text{S.CH}_2\text{CO}_2\text{O}$, m. 145°. This lactone was also obtained in a separate exp.

from the two acids with which it is here associated. Thionylidiacetic acid treated with Br gave a mixt. of $(\text{CHBr}_2)_2\text{SO}$, m. 52°, and $(\text{CHBr}_2)_2\text{SO}_2$, m. 161°, and the tribasic acid. When $\text{S}(\text{CH}_2\text{CO}_2\text{Et})_2$ was used the corresponding ester, $(\text{EtO}_2\text{CCH}_2)_2\text{SO}$ was formed by the H_2O_2 oxidation. The medium in this case was glacial AcOH . This compd. was treated with HCl and gave glyoxylic, thioglycolic, and the tribasic acid. An attempt was made to make this ester by treating the acid in alc. with dry HCl. The result was a compd. with one Cl substituted in an α -position in $(\text{EtO}_2\text{CCH}_2)_2\text{S}$. This substance is not sol. in concd. HCl but is sol. in petroleum ether. When it was boiled in Ac_2O , AcO replaced the Cl. This compd. was also insol. in HCl but sol. in petroleum ether. (Cf. Pummerer, C. A. 4, 3486.)

A. R. ROSE

The nature of the reaction in the synthesis of acetoacetic ester. H. SCHREIBLER. *Z. angew. Chem.* 36, 6-8(1923).—S. explains the acetoacetic ester synthesis on the basis of the following reactions: (1) $\text{AcOEt} + \text{Na} \longrightarrow \text{CH}_2\text{:C}(\text{OEt})\text{ONa} + \text{H}$; (2) $\text{AcOEt} + \text{CH}_2\text{:C}(\text{OEt})\text{ONa} \longrightarrow \text{AcOCH}_2\text{C}(\text{OEt})_2\text{ONa}$. The last compd. gives: (1) acetoacetic ester and EtOH with dil. acids; (2) ketene acetal $(\text{CH}_2\text{:C}(\text{OEt})\text{OH})$ and AcONa by spontaneous decompn.; (3) Me_2CO , EtOH, and NaHCO_3 by the slow action of heat and H_2O . The assumption of the formation of this intermediate compd. explains the fact that ketene acetal and AcONa are by-products of the acetoacetic acid ester synthesis.

T. S. CARSWELL

Urethans from chlorine-substituted secondary and tertiary alcohols. LESTER YODER. *J. Am. Chem. Soc.* **45**, 475-9 (1923).—*Trichloromethyl-dimethylcarbinyl carbamate* (A), $\text{H}_2\text{NCO}_2\text{CMe}_2\text{CCl}_3$, from chlorotone and Na in CaH_2 poured into COCl_2 in PhMe and then treated with an excess of NH_3 , m. 102° . *Trichloromethyl-phenylcarbinyl carbamate*, similarly prep'd. from $\text{CCl}_3\text{CHPhOH}$, m. 127° . *Trichloromethyl-dimethylcarbinyl carbamate*, prep'd. like A with PhNH_2 instead of NH_3 , m. 118° . *Dichloromethyl-dimethylcarbinyl carbamate*, from $\text{Cl}_2\text{CHCMe}_2\text{MgBr}$ treated with COCl_2 and subsequently with NH_4OH , m. 122° . *Trichloromethyl-methylcarbinyl carbamate* (B), from $\text{CCl}_3\text{CHMeMgBr}$, m. 125° . Glycerol, $\text{CCl}_3\text{CH}(\text{OH})_2$ and ZnCl_2 at 130° under pressure give an alc. (C), probably *2-trichloromethyl-1,4-dioxolane-4-carbinol* (*trichloroethylideneglycerol*), $\text{O.CH}(\text{CCl}_3).\text{O.CH}_2\text{CHCH}_2\text{OH}$, b_{19} $125-8^\circ$, whose car-

bamate m. 114° . The above carbamates are tasteless and odorless, very slightly sol. in H_2O , quite stable in boiling H_2O but decomp'd. by strong acids and alkalis. A and B are strong hypnotics; C has a pleasant odor, a sweet slightly burning taste and a marked fleeting hypnotic effect.

C. A. R.

Synthesis of urea with the enzyme urease. EDWARD MACK AND D. S. VILLARS. *J. Am. Chem. Soc.* **45**, 501-5 (1923).—When conc'd. solns. of NH_4 carbonate and carbamate are used, urease acts reversibly, increasing the velocity of formation of urea and hastening the attainment of equil. A 1% soln. of the urease will bring about equil. in a 10 *N* carbonate-carbamate soln. contg. about equal amts. of each salt in about 10 hrs. at 55° , the optimum temp. for urease; with a 0.1% soln. of urease the reaction is about $1/2$ complete in 98 hrs.; without urease, equil. would be attained in only about 600 days. The amts. of urea at equil. (det'd. by the Fossé method by pptn. with xanthidrol) were approx. the same as those found by Lewis and Burrows (C. A. 7, 470).

C. A. R.

The action of urease in the decomposition of urea. EDWARD MACK AND D. S. VILLARS. *J. Am. Chem. Soc.* **45**, 565-10 (1923).—Exptl. data are presented to show that the transformation of NH_4CNO into urea is not catalyzed by urease. When urea is hydrolyzed, in the presence of urease, into $\text{NH}_4\text{CO}_2\text{NH}_4$, which then changes into $(\text{NH}_4)_2\text{CO}_3$, there is a simultaneous formation of NH_4CNO from the urea. By a process of elimination it is shown that the particular reaction stage catalyzed by urease is the transformation of urea into $\text{NH}_4\text{CO}_2\text{NH}_4$.

C. A. R.

Urea and guanidine derivatives of sulfo fatty acids. RUDOLF ANDREASCH. *Monatsh.* **43**, 485-91 (1923); cf. *Ibid* **1**, 446.—*Barium sulfoacetylurea*, 4- or 6 sided plates from H_2O . *Copper salt*, sky-blue needles. *Ammonium salt*, rhombic leaflets. The K salt is also obtained by the interaction of $\text{H}_2\text{NCONHCOCH}_2\text{Cl}$ and K_2SO_4 , KCl being split off. *Sulfoacetyl-methylurea*, $\text{MeNHCONHCOCH}_2\text{SO}_3\text{H}$, isolated as the *potassium salt*, long, fine needles, contg. 1 H_2O of crystn. *Chloroacetyl-ethylurea*, fine needles, m. 138° . With K_2SO_4 this gives the *potassium salt* of *sulf. acetyl-ethylurea*, which is very sol. and was transformed into the *barium salt*, large glistening needles with 1 H_2O , for analysis. *Potassium salt* of *sulfoacetyl-phenylurea*, fine scales. *Sulfoacetyl-guanidine*, $(\text{HN}:\text{C.NH}_2.\text{O.SO}_2\text{CH}_2\text{CO.NH})_2$, sandy powder which turns brown at 230° ; the au-

soln. reacts neutral, which indicates a union between the NH_2 and SO_3H groups. *Chloroacetyl-di-phenylurea*, $\text{PhNHCONHCOCH}_2\text{Cl}$, 4-sided plates, m. 180° . *Sulfoisovalerylurea*, $\text{Me}_2\text{CHCH}(\text{SO}_3\text{H})\text{CONHCONH}_2$, by boiling bromural with $(\text{NH}_4)_2\text{SO}_4$, and analyzed as the *ammonium salt*, rhombic plates; a by-product appears to be isovalerylurea.

C. J. WEST

Dithiocarbazine acid. II. S. M. LOSANITCH. *Glas. Acad. Sci. Belgrade* **103**, 1-9 (1922); cf. C. A. **15**, 2829; **17**, 534.—Previously, it was shown that the dithiocarbazines decomp. slowly when heated in aq. or alc. soln., yielding H_2S , $(\text{NH}_4)_2\text{S}$,

NH_3 (or an amine), S, and a white, cryst. product of acid reaction. This decompn. yields in the beginning H_2S , semithiocarbazide, and thiocarbazide. Subsequently, the products of the 1st decompn. interact with the dithiocarbazinate and form NH_3 and thiodisemithiocarbazide, $\text{NH}_2\text{NHCSSCSNHNH}_2$, which then suffers transformation into the white, cryst. acid product mentioned in *C. A.* 15, 2829. For this compd. L. suggests the constitution $\text{S}[\text{C}(\text{SH})\text{:NNH}_2]_2$ or $\text{S}(\text{C:N.NH}_2\text{S})_2$, while Busch, who

obtained it previously, regarded it as a deriv. of thiodiazole of the formula $\text{S.C}(\text{SH})\text{:N.N:C.SH.N}_2\text{H}_4$ [cf. *Ber.* 27, 2507-20; *J. prakt. Chem.* [II] 60, 25-55(1899)].

It forms needles and plates, decomp. about 170° , m. 225° , and is sol. in water, less so in alc. With MeI , it yields a dimethyl ester, colorless crystals, m. $136-7^\circ$. It also forms a mono-, di-, and polysulfide. The disulfide has been described by Ziegele [*J. prakt. Chem.* [II] 60, 25-55(1899)]. The monosulfide is formed if the aq. or alc. soln. of the acid is boiled; it crystals in yellow needles, m. 178° (decompn.), and forms salts with bases. The salts of the alkalis and NH_4 are sol. in water; those of the heavy metals insol. The NH_4 salt yields with MeI the monosulfide methyl ester, a white substance, sol. in alcohol, m. 71° . The polysulfide, $(\text{C}_6\text{H}_5\text{N}_2\text{S})_n$, is formed together with the disulfide by the method employed by Ziegele (*loc. cit.*); it is insol. even in boiling alc., forms yellow crystals, m. 186° , and is not identical with the polysulfide $(\text{C}_6\text{H}_5\text{N}_2\text{S}_2)_n$ described by Ziegele. J. C. S.

Disubstituted guanidines. WINFIELD SCOTT. *Ind. Eng. Chem.* 15, 286-90 (1923).—Diphenylguanidine (A) reacts with carbodiphenylimide to form tetraphenylbiguanide, needles from alc., m. 136° ; hydrochloride, sol. in alc., insol. in H_2O . A also reacts with H_2S and CS_2 to form diphenylguanidine trithiocarbonate (C), orange-yellow needles from aq. Me_2CO , m. $88-9^\circ$ (decompn.). C with ice and strong HCl liberates trithiocarbonic acid. The polymerizing action of Zn compds. during vulcanization is marked in connection with disubstituted guanidines. The accelerating action of di-*p*-tolylguanidine, di-*o*-tolylguanidine (D), and A is in the order named, the 1st being strongest. Expt. showed that 4 parts of D were equiv. to 5 parts of A. The use of $(\text{PhNH})_2\text{CH}_2$ in connection with D retarded the rate of vulcanization in the initial stages, unless the $(\text{PhNH})_2\text{CH}_2$ was compensated for by an increase in S. T. S. CARSWELL

Isopropylmalonic acid derivatives and steric hindrance. F. PREISWERR. *Helvetica Chim. Acta* 6, 192-8(1923).—The abnormal behavior of compds. containing an iso-Pr group (cf. Fischer and Scheibler, *C. A.* 2, 1696; Sachs and Weigert, *C. A.* 2, 410; Fischer, Holzappel and Gwinner, *C. A.* 6, 1003; Karrer *et al.*, *C. A.* 16, 3870) is usually explained as due to steric hindrance. This is not the case with the further alkylation of $\text{Me}_2\text{CHCH}(\text{CO}_2\text{Et})_2$ (A), $\text{Me}_2\text{CHCH}(\text{CN})\text{CO}_2\text{Et}$ (B) and isopropylbarbituric acid (C) where the iso-Pr group occupies the same position relative to the labile H atom. The introduction of 1 alkyl group in barbituric acid (D) renders the methylene H atom more reactive; the same group reduces the acidity more than a Pr group and therefore C is more readily alkylated than are other monoalkylbarbituric acids (cf. Fischer and Dilthey, *Ann.* 335, 357(1904)). The introduction of one iso-Pr group in $\text{NCCCH}_2\text{CO}_2\text{Et}$ (E) causes very little reduction in its acidity and is therefore without influence in further alkylation of the methylene H atom. Malonic ester (F) is less acidic than either D or E, but is sufficiently acidic to permit the introduction of 1 alkyl group on the methylene C atom; when the acidity is slightly reduced by the introduction of 1 group it becomes very difficult to replace the 2nd H atom. The iso-Pr group reduces the acidity to such a degree that it becomes impossible to alkylate further. Isopropylmethylbarbituric acid was prepd. by warming to 40° and stirring for 24 hrs. a mixt. of 85 g. C, 305 g. 6.7% NaOH and 75 g. MeI , filtering and recrystg. the ppt. from EtOH ; it is insol. in H_2O and m. $186-7^\circ$. Isopropylallylbarbituric acid was prepd. by adding

to 85 g. C in 250 cc. H₂O the calcd. amt. of 30% NaOH, then 65 g. allyl bromide, and stirring the mixt. at 25–30° for 12 hrs.; the crystals from EtOH-H₂O are readily sol. in EtOH, Et₂O or PhH, slightly sol. in H₂O and m. 137–8°. *Diisopropylbarbituric acid*, similarly prepd. from C in NaOH and Me₂CHBr at 55–60° for 48 hrs., was purified by dissolving the ppt. in cold, dil. NaOH, reprecip. with CO₂ and recrystg. from EtOH-AcOH; it is neutral to litmus, slightly sol. in EtOH, very slightly sol. in H₂O and m. 230° (decompn.).

N. A. LANGE

Thermal decomposition of dicarboxylic acids. A. WINDAUS AND M. EHRENSTEIN. *Nach. kgl. Ges. Wiss. Göttingen, Math-Phys. Klasse* 1922, 1–7.—W. and E. test again the validity of Blanc's rule according to which pimelic and adipic acids heated to 300° yield cyclic ketones, glutaric and succinic acids and their anhydrides, a principle applicable to constitution studies. These products and the Ba salts of the acids were heated above the decompn. temps. to det. whether cyclic ketones are obtained or not. Ba salts of β,β -dimethylglutaric acid heated dry yielded especially acetone, mesityl oxide and isophorone, each of which was definitely identified. The formation of acetone is explained experimentally by the reaction at high temps. between mesityl oxide and BaCO₃ in the presence of traces of water [Me₂C:CHCOMe + H₂O \rightleftharpoons 2MeCCOMe]; the formation of mesityl oxide from the decompn. of primarily formed dimethylcyclobutanone; and the formation of isophorone from autocondensation of acetone with mesityl oxide. *cis*-Hexahydrophthalic anhydride heated to 380° yielded

$$\text{CO}_2, \begin{array}{c} \text{CH}_2\text{CH}_2\text{CHCO}- \\ | \\ \text{CH}_2\text{CH}_2\text{CH}- \end{array} \quad (\text{which forms a double mol. of dodecahydro-anthraquinone}),$$

anthraquinones, and hydrated anthracenes contg. some C₁₄H₁₀ and C₁₄H₁₂.

I. NEWTON KUGELMASS

Ring-chain tautomerism. IV. The effect of the methyl ethyl grouping on the carbon tetrahedral angle. BALBIR SINGH AND J. F. THORPE. *J. Chem. Soc.* 123, 113–22(1923); cf. *C. A.* 16, 4187.—The differences observed between the Me₂ and Et₂ series must rest on the small difference of angle in the 2 series and in order to study the effect produced by diminishing this difference comparative expts. in the MeEt series have been carried out. *Methylethylglutaric anhydride*, m. about 25°; *anilic acid*, m. 105°. *trans- α,α' -Dibromo- β,β -methylglutaric acid*, by brominating the acid chloride and pouring into HCO₂H; the 1st crop of crystals consists almost exclusively of the *trans*-isomer, m. 173° (decompn.). The *cis*-isomer, purified by crystn. from C₆H₆ and CHCl₃-petr. ether, m. 146°. The Et ester loses EtBr on distn. under 31 mm. and gives *methylethylglutaric bromo-lactonic ester*, EtMeC.CH(CO₂Et).O.CO.CHBr, b₃₁ 194–6°. The acid

ester also decomps. on distn. Both the *cis*- and the *trans*-acids yield on treatment with Na₂CO₃ the same *trans*-lactonic acid of α,α' -dihydroxy- β,β -methylethylglutaric acid, m. 116°; it is not changed by heating with 64% KOH but higher concns. decompd. the acid, giving, among other products, (CO₂H)₂. *Acetate*, small needles, m. 121°. The action of EtOH-KOH upon the crude EtBr₂-ester gave *i*-ethoxy-3-methyl-3-ethylcyclopropane-1,2-dicarboxylic acid, m. 150°. The stability of this acid is remarkable, it being unaffected by concd. aq. KOH even on prolonged boiling and by concd. HCl. Gentle heating with 80% H₂SO₄ gave HO₂CCMe.CEtCO₂H, while boiling with HI gave a small amt. of *trans*-3-methyl-3-ethylcyclopropane-1,2-dicarboxylic acid (A), m. 221°. *Silver salt*, white powder. *Dianilide*, light scales, m. 291°. The action of MeOH-KOH on the Br₂-ester gave α,α' -dihydroxy- β,β -methylethylglutaric acid, sepd. by pptg. the Ca salt in Et₂O, long needles, m. 80°. *Silver salt*. The other product of the reaction was *i*-methoxy-3-methyl-3-ethylcyclopropane-1,2-dicarboxylic acid, which was sepd. by crystn. from CHCl₃ into the *trans*-acid, m. 149°, and the *cis*-acid, m. 141°. Both acids yield the same *anhydride*, b₇ 144°; upon hydration the *cis*-acid is formed, so that the *trans*-

acid is converted into the *cis*-acid in this manner. Hydrolysis of the MeO deriv. with HI gave α -keto- β , β -methylthylglutaric acid, characterized by the quinoxaline, m. 216°. These expts. show that the alteration of the tetrahedral angle causes the keto acid and HO-ring acid to be tautomeric in the case of the *gem*-Et₂ compd., causes also the HO-ring acid to be the only stable form in the cyclohexane series, and the keto acid the only stable form in the *gem*-Me₂ series. The hydrolysis of the EtBr-ester gave A and the *cis*-isomer, m. 180° (decompn.), also prepd. by heating the *trans*-isomer with Ac₂O. The *anhydride*, prepd. by heating the acid above its m. p., was characterized by conversion into the *anilic acid*, m. 193° (decompn.). C. J. WEST

Glutaconic acids. XIII. The isomerism due to retarded mobility. JOCELYN F. THORPE AND ARTHUR S. WOOD. *J. Chem. Soc.* 123, 62-4(1923); cf. *C. A.* 15, 2070.—Polemical; cf. Feist, *C. A.* 16, 2307. T. and W. believe that a glutaconic acid, in which the presence of groups in the 3-C system so far retards the movement of the tautomeric H atoms as to enable it to remain within either the 3-C system or 1 or other of the systems C.C.O., can be isolated in 5 forms—2 *trans*, 2 *cis*, and 1 "normal." C. J. W.

Characterization of alkylglycerols. RAYMOND DELABY. *Compt. rend.* 176, 398-9 (1923).—A study of the reactions proposed by Denigès (*Précis de Chimie analytique* 1920, p. 151) indicates that, while a few only distinguish glycerol from its higher homologs, these are sufficient for rigorous identification. After oxidation with Br and dehydration with H₂SO₄, glycerol (A), methyl- (B), ethyl- (C), propyl- (D), and butylglycerol (E) give color reactions with certain alkaloids and phenols. Of codcine (F), resorcinol, thymol, and β -naphthol, only F differentiates clearly by color and spectroscopic test, giving with A blue tinged with green, with B clear olive-green, with C dark brown-mahogany, with D clear brown-mahogany, with E orange-yellow. If to the brominated solns., KBr is added before the addn. of H₂SO₄, the blue color given with guaiacol distinguishes A from its homologs (B gives a violet, C, D and E a blackish coloration). Less distinctive colors are given by salicylic acid and Me salicylate. The cryst. osazone of the dihydroxyacetone from A, prepd. directly from the oxidation liquor, differs decidedly from that of B, forming prismatic needles radiating from a center. The higher members are oily. By distn. of the oxidation liquors with H₂SO₄ and prepn. of the osazone of the distillate, the alkylglyoxal osazone from B seps. as fern leaves, that from C as grouped needles, sometimes having rounded club-like ends; those from D and E are oily. All these oxidation products reduce Nessler, Fehling and NH₃-AgNO₃ solns. The oxidation products formed from these alcs. by KMnO₄ yield no distinctive reactions under the above conditions. Oxidation by PbO₂ causes rupture of the chain, forming CO₂ and HCHO, with increasing difficulty with the higher members, but in no case are specific reactions found. I. P. ROLF

Relation between the crystal structure and the constitution of carbon compounds. I. Compounds of the type CX₄. ISABEL E. KNAGGS. *J. Chem. Soc.* 123, 71-9(1923).—K. discusses the subject from the working hypothesis that the most sym. mol. structure should give rise to the most sym. crystallographic forms; i. e., the type CX₄, where X is an element or sym. group like Me, should give rise to crystals of the cubic system, while compds. in which X is a less sym. group should give rise to tetragonal crystals. Several compds. are discussed and modifications necessary in the detailed application of the hypothesis noted. Full crystallographic data are given for *pentaerythritol tetrannitrate* and *tetracetate* and for *methanetetraacetic acid*. C. J. WEST

Carbohydrates. II. A new anhydride of glucose. PERCY BRIGL. *Z. physiol. Chem.* 122, 245-62(1922).—Glucose 1,2-anhydride 3,5,6-triacetate, CH₂(OAc)-

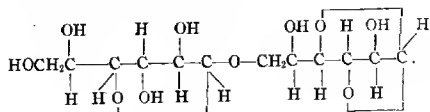
CH(OAc) $\overset{\text{O}}{\text{CH}}\text{CH}(\text{OAc})\text{CH}_2\text{CH}_2\text{O}$, was prepd. by suspending 10 g. of triacetochloro-glucose in 50 cc. of dry C₆H₆ and passing in dry NH₃ for 2-3 hrs.; finally the

reaction mixt. was stoppered and shaken for 2 hrs. The pptd. NH_4Cl was filtered and NH_3 removed from the filtrate in a vacuum over H_2SO_4 . Before the desired product could be crystd. a difficultly sol. Cl-contg. compd. had to be sepd. by adding the soln. to 75 cc. of petroleum ether, whereupon the cryst. impurity, together with an oil contg. some of the desired anhydride, pptd. This filtrate was evapd. in a vacuum and again pptd. with petroleum ether. Crystn. of the oil which sepd. was facilitated by seeding. The product was purified by dissolving in C_6H_6 and pptg. with petr. ether; white, oblique plates, m. 59.5° , sol. in most org. solvents except petroleum ether and CS_2 , $[\alpha]_D^{18}$ 108.5° , heat of combustion 4595 cal. per g. With Ac_2O a mixt. contg. α -pentaacetylglucose was obtained. On treatment with H_2O 3,5,6-glucose triacetate (A) was formed; only the β -form appears to result primarily. The α -form m. $113-5^\circ$, is sol. in H_2O and in liquids miscible with H_2O and almost insol. in cold C_6H_6 and Et_2O . If the anhydride is treated with MeOH instead of H_2O it gives β -methyl glucoside 3,5,6-triacetate, compact needles, m. $96-8^\circ$, with the same solubilities as A. R. L. STREHL

Crystalline glucose-ammonia and isoglucosamine. A. R. LING AND D. R. NANJL. *J. Chem. Soc.* 121, 1682-3(1922); cf. *C. A.* 17, 1215.—The product formed by the action of NH_3 on dextrose in MeOH is the same as in H_2O , i. e., glucose-ammonia. This was confirmed by reduction to glucamine (H with Ni catalyst, Al-Hg in MeOH at 40° and electrolytic) and by the prepn. of the condensation product, $\text{C}_9\text{H}_{16}\text{O}_5\text{NSNa}$, with $\text{HCHO} \cdot \text{NaHSO}_3$ hard, amorphous mass, which is very hygroscopic. Recrystd. from 95% MeOH , isoglucosamine results (*C. A.* 7, 1709). C. J. WEST

Carob-tree manna and its sugar. Identity of this sugar with pinitol or methyl-d-inositol. C. CHAUAUX. *Bull. soc. chim. biol.* 4, 597-600(1922).—The manna of the carob tree (*Ceratonia siliqua* L.) has the following % compn.: H_2O , 3; debris of bark, and impurities insol. in H_2O and EtOH , 2; tannin, 3.5; reducing material, 0.7; cryst. sugar 84.0; undetd. 6.8. The sugar can be completely extd. by boiling with 95% EtOH , and seps. on cooling. It is still colored, and the color is not removed by recrystn. It is obtained pure and colorless by treating the manna with boiling H_2O , filtering, adding to the filtrate excess of basic Pb acetate, filtering, and removing Pb with H_2S , concg. to a sirup, and adding boiling 95% EtOH . The pure sugar seps. on cooling. It is identical with the methyl-d-inositol from *Pinus lambertiana*. A. T. CAMERON

Maltosan. AMÉ PICTET AND ANDRÉ MARFORT. *Helvetica Chim. Acta* 6, 129-33 (1923).—The maltosan was prepd. by heating maltose at atm. pressure to $140-5^\circ$ until it had lost the H_2O of crystn., after which the pressure was gradually reduced to 15 mm. and the temp. raised to 160° ; after many hrs. there is obtained a brittle, porous substance, $\text{C}_{12}\text{H}_{20}\text{O}_{10}$, softens 120° , m. about $145-50^\circ$, decomps. on distn. under 2 mm., is very sol. in cold H_2O , fairly sol. in MeOH , $\text{C}_6\text{H}_5\text{N}$ or hot AcOH and insol. in other org. solvents; the value $[\alpha]_D^{20}$ 75.8° remains unchanged after boiling 4 hrs. with H_2O , showing that maltose is not formed by hydrolysis; it reduces hot Fehling soln. to the same degree as maltose and yields with PhN_2H_3 the same osazone, m. 206° , decolorizes cold, neutral KMnO_4 , is fermented by yeast; heated with NaOAc and Ac_2O , it gives a hexaacetate, m. 95° , dissolved in concd. HCl , it yields a hydrochloride, $\text{C}_{12}\text{H}_{20}\text{O}_6\text{Cl}$, which in 90% cold EtOH with MeONa in MeOH gives β -methyl maltoside, m. 95° (decompn.), $[\alpha]$ 70.7° (cf. Fischer and Armstrong, *Ber.* 34, 2896(1901); Königs and Kuerr, *Ber.* 34, 4346(1901)). The formula proposed for the maltosan is



The results obtained in a similar manner with sucrose and lactose are incomplete and will be reported later.

N. A. LANGE

Cellulose chemistry. III. Parabromoacetaldehyde and monobromoacetaldehyde. Their preparation, properties and utilization for the synthesis of bromo- and hydroxy-cyclic acetals related to polysaccharides. HAROLD HIBBERT AND H. S. HILL. *J. Am. Chem. Soc.* **45**, 734-51 (1923); cf. *C. A.* **17**, 540.—*Parabromoacetaldehyde*, obtained in 32% yield from paraldehyde with Br in sunlight at -5° to -10° and subsequent treatment with NaOAc, m. 104° , depolymerizes at about 165° into *bromoacetaldehyde*, h. $107-12^{\circ}$, whose *semicarbazone* m. about 128° (decompn.) and which on standing, more rapidly in the presence of concd. acids, polymerizes back to the trimer. The crude product resulting from the bromination of paraldehyde may be used for the prepn. of cyclic acetals by condensation with polyals. Thus, with α -bromohydrin, b₁₂ 127° , is obtained *bromoethylidene bromohydrin*, $\text{BrCH}_2\text{CH}(\text{CH}_2\text{OCH}(\text{CH}_2\text{Br})\text{O})_2$, b₁₀ $118-20^{\circ}$,

and with $(\text{CH}_2\text{OH})_2$ *bromoethylidene glycol*, $\text{CH}_2\text{CH}_2\text{OCH}(\text{CH}_2\text{Br})\text{O}$, h₁₂ $63-5^{\circ}$, b.

175° . *Bromoethylidenetrimethylene glycol*, b. $191-4^{\circ}$. *Bromoethylideneglycerol*, $\text{HOCH}_2\text{CH}(\text{CH}_2\text{OCH}(\text{CH}_2\text{Br})\text{O})_2$ or $\text{HOCH}(\text{CH}_2\text{O})_2\text{CHCH}_2\text{Br}$, b₁₂ $137-40^{\circ}$; heated

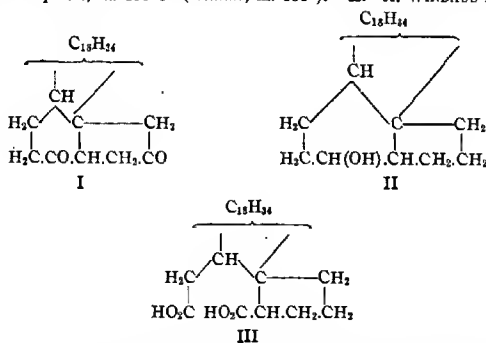
with aq. KOH it loses all its Br and gives 2 products, which are probably the *bicyclic lactonyl derivative* $\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$, m. about 39° , and *hydroxyethylidene-*

glycerol, h₁₁ 145° . *Di[bromoethylidene]mannitol*, $[\text{CH}(\text{OH})\text{CH}(\text{CH}_2\text{OCH}(\text{CH}_2\text{Br})\text{O})_2]$

(?), m. $137-41^{\circ}$. *Ethylidene bromohydrin*, from α -bromohydrin, AcH and a trace of I, b. $168-9^{\circ}$.

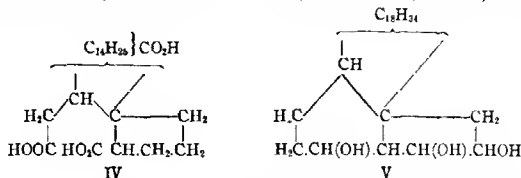
C. A. R.

Cholesterol. I. A. WINDAUS AND HARRY GRIMMEL. *Z. physiol. Chem.* **117**, 146-58 (1921); cf. *C. A.* **14**, 1933, 3083, 3084, 3649; **15**, 3279.—The ketodicarboxylic acid, $\text{C}_{27}\text{H}_{44}\text{O}_8$, formed by the oxidation of cholestan-4,7-dione (I) forms a *semicarbazide* (slender needles, m. 240°) which with NaOEt and alc. yields an acid, $\text{C}_{27}\text{H}_{46}\text{O}_8$, identical with an acid obtained by the oxidation of dihydrocholesterol (II); it therefore has the constitution III. This is confirmed by the fact that when heated it forms a *diketone*, $\text{C}_{26}\text{H}_{42}\text{O}_2$, small plates, m. $148-9^{\circ}$ (*dioxime*, m. 191°). **II.** A. WINDAUS AND A. VON



STADEN.—From the dicarboxylic acid, $\text{C}_{27}\text{H}_{46}\text{O}_8$ (III), a *tricarboxylic acid*, $\text{C}_{28}\text{H}_{48}\text{O}_9$, has been prepd. by oxidation with CrO_3 ; it crystallizes from AcOH in rosetts of slender needles, m. 238° , and forms a *trimethyl ester*, rectangular leaflets, m. $86-7^{\circ}$. This acid

apparently has the constitution IV. III. A. WINDAUS AND H. LÜBERS.—On boiling α -cholestantriol (V) (Pickard and Yates, *C. A.* 3, 2679; Windaus, *C. A.* 9, 2535) with



HCl in MeOH, it is converted into the *chlorohydrin* of α -cholesterol oxide, $\text{C}_{27}\text{H}_{47}\text{O}_2\text{Cl}$, long needles; m. $170-1^\circ$. With alc. KOH, or with acid, β -cholesterol oxide is obtained, identical with that isolated by Westphalen (*C. A.* 9, 2535). J. C. S.

Identity of xanthosterol with lupeol. A. J. ULTÉ. *Bull. jardin bot. Buitenzorg* 4, (iii) 315(1922); cf. Dieterle, *C. A.* 16, 2487.—The phytosterol isolated by Dieterle (*C. A.* 14, 1871) from *Xanthoxylon budrunga* has been re-obtained, and proves to be identical with lupeol as already suggested by Goodson (*C. A.* 15, 2468). Oestling's phytosterol (*C. A.* 9, 351) from *Fagara xanthoxyloides*, Lam. (*X. senegalense*, DC.) is also lupeol. J. C. S.

β -Amyrin from Manila elemi resin. ALEXANDER ROLLETT. *Monatsh.* 43, 413-7 (1923); cf. *C. A.* 15, 1016; 16, 2323.—The bromination of β -amyrin in AcOH gave a mixt. of *bromo- β -amyrin acetate*, $\text{C}_{30}\text{H}_{50}\text{O}_2\text{Br}$, m. $235-6^\circ$ (the concd. H_2SO_4 soln. is yellow with a green fluorescence), and a *dibromo- β -amyrin*, $\text{C}_{30}\text{H}_{48}(\text{OH})\text{Br}_2$, m. $210-6^\circ$ (decompn.), which remains in the AcOH mother liquor. Oxidation of β -amyrin with CrO_3 in AcOH gives *β -amyranone (amyrone)*, m. $177-9^\circ$; *oxime*, m. $265-7^\circ$. Further oxidation with KMnO_4 produced no effect. Heated with BzCl at 200° , it gives *β -amyrenal benzoate*, needles, m. $181-2^\circ$, which, on sapon., gives amyrene, m. 174° . C. J. W.

Formation and stability of spiro compounds. X. Spiro compounds derived from cycloheptane. J. W. BAKER AND C. K. INGOLD. *J. Chem. Soc.* 123, 122-33(1923); cf. *C. A.* 16, 4191.—The general investigation of ring formation has now reached the point where it is necessary more closely to exam. individual cases in which real or apparent exceptions to the general hypothesis might possibly be found. The present work deals with expts. on the effect of including 2 valencies of a C atom in rings contg. a large no. of atoms. There appears to exist some condition in the cycloheptane ring which greatly reduces the strain within the ring and therefore the convergence towards one another of the 2 AcOH residues. The effect of this ring in promoting the formation and in enhancing the stability of the spirane structures is not only less than it might be expected to be but is actually somewhat less than that which the cyclohexane ring has been shown to exert. In many respects, however, the results are closely similar to those obtained with the cyclohexane ring. One of the striking characteristics of the heptane series is their remarkable lack of tendency to crystallize. *Ethyl hydrogen α -bromocycloheptane-1,1-diacetate* (A), $(\text{CH}_2)_5\text{C}(\text{CHBrCO}_2\text{H})\text{CH}_2\text{CO}_2\text{Et}$, obtained in 60% yield on monobromination and in 25% yield on dibromination, needles, m. $84-5^\circ$. *Ethyl- α,α' -dibromocycloheptane-1,1-diacetate* (B) could not be purified, for on distn. it yields the *lactone of ethyl hydrogen α -bromo- α' -hydroxycycloheptane-1,1-diacetate*, $(\text{CH}_2)_5\text{C}(\text{CHBr}.\text{CO.O}.\text{CH}.$

$\text{CO}_2\text{Et})$ (C), viscous oil, $b_{28} 230-4^\circ$. Hydrolysis of A with 64% KOH gave *trans-cycloheptanespirocyclopropane-2,3-dicarboxylic acid*, small needles, m. 235° , which is stable towards 5% HCl at 200° but is completely decompd. by 20% HCl at 240° , and *α -hydroxycycloheptane-1,1-diacetic lactone* (which is the only product of the hydrolysis with aq. Na_2CO_3), viscous gum, $b_{20} 240-5^\circ$; this titrated as a monobasic acid, but the free

acid was unstable and was analyzed as the *silver salt*. The hydrolysis of C gave: (1) α, α' -dihydroxycycloheptane-1,1-diacetic lactone (about 90% of the reaction product) viscous liquid, b_{10} 263-7°; this has a powerful, characteristic odor resembling decaying coconuts. *Silver salt*. The corresponding acid was analyzed as the *disilver salt*. (2) *Cycloheptylideneacetic acid*, $(CH_2)_6C:CHCO_2H$, found in the "low" fraction in the distn. of the lactone (7% yield), b_{10} 158°. It instantly decolorizes cold alk. $KMnO_4$ and absorbs Br. *Silver salt*. *Dibromide*, m. 124-5°. (3) *Cycloheptanespirocyclopropane-2-ol-2,3-dicarboxylic acid*, cubical crystals, m. 195°. This gives no color with $FeCl_3$ and is stable towards $KMnO_4$ and Br. $(CO_2H)_2$ was also recognized in the hydrolysis product.

C. J. WEST

Pinacol rearrangement. V. Reciprocal transformation of compounds with six- and seven-membered carbon rings. HANS MEERWEIN AND JOSEPH SCHÄFER. *J. prakt. Chem.* 104, 289-310(1922); cf. *C. A.* 13, 1831.—The mixt. of ketones obtained by the rearrangement of *asym*-dimethylpentamethyleneglycol was treated with $NaOBr$, and the alk. soln. extd. with Et_2O ; the ketone was then purified through the semicarbazone, finally giving 2,2-dimethylcycloheptanone, h. 190°. Na and $EtOH$ reduce this to 2,2-dimethylcycloheptanol (A), b_{13} 76.8-7.2°, the phenylurethan of which forms long needles, m. 100-1°. 1,1-Methylacetylcyclohexane was obtained by the action of $MeMgI$ upon the corresponding acid chloride, and h. 186.5-7°. Reduction gave 1,1-methyl- α -hydroxyethylcyclohexane (B), viscous oil, b_{13} 87.5°. The phenylurethan did not crystallize. Heated with $ZnCl_2$ at 180° for 20 min., each alc. yielded a mixt. of 1,1-dimethylcycloheptene and 1-isopropylcyclohexene. In the case of A, the ratio was approx. 2 to 1; in that of B about 1 to 1.

C. J. WEST

Cymene as a by-product in the distillation of wood. EMIL HEUSER, L. ZEH AND B. ASCHAN. *Z. angew. Chem.* 36, 37-8(1923).—Wood was hydrolyzed by heating in an autoclave under 7-8 atm. for 30 min. with dil. acid, and the volatile matter removed by flowing off the autoclave. The volatile portion was condensed, when light oil sepd. from the aq. distillate. The light oil was washed with $NaHSO_3$ to remove furfural, and then with acid and H_2O . The residue was fractionated, and the portion h. 171-84° collected and sulfonated with oleum. From the sulfonated product *p*-cymenesulfonic acid was obtained. The total content of *p*-cymene in the light oil amounted to 4-5%.

T. S. CARSWELL

Condensation products of phenylhydroxylamine with hydroxymethylene compounds and carbinols. IV(?). Hydroxymethylenephénylacetic ester and hydroxymethylenephényl cyanide and phenylhydroxylamine. H. RUPE AND J. GRÜNHOLZ. *Helvetica Chim. Acta* 6, 102-10(1923); cf. *C. A.* 16, 1938; 17, 1006.—The condensation of $HOCH:CPhCO_2Et$ (A) (cf. Wislicenus, *Ann.* 291, 164(1896)) and $PhNHOH$ (B) yields an intermediate compd. (C) which is too unstable for isolation, losing a mol. of $EtOH$ to form β, N -di β -phenylisoxazalone (D). $HCOCH:CPhCO_2Et$ does not react with B. The Me ester of A similarly yields D. B and $HOCH:CPhCN$ (I) condense to form α -cyanostyrylphenylhydroxylamine, which could not be hydrolyzed to the corresponding acid. 14 g. A and 8 g. B in 45 cc. $EtOH$ were warmed on a water bath until $FeCl_3$ no longer gave a test for A; the crystals of D, which sep. in 75% yield, are slightly sol. in $EtOH$, $CHCl_3$ or Et_2O and insol. in petr. ether and PhH ; they form needles from $EtOH$, m. 175°; condensation may also be effected by warming a mixt. of A and B directly or in $AcOH$ at room temp.; dil. acids, aq. alkalis and PhN_2H_3 have no action on D. 0.2 g. D in ice-cold dry $CHCl_3$ were treated in sunlight with 0.04 g. Br_2 in $CHCl_3$; the β, γ -dibromo addition compound which seps. after several hrs., when filtered, washed with $CHCl_3$ and dried over $CaCl_2$ and paraffin, m. 180°; attempts to recryst. gave decompn. with evolution of HBr , forming a γ -monobromo derivative, m. 164-6° (decompn.), slightly sol. in $EtOH$, Et_2O or petr. ether and readily sol. in hot PhH or $CHCl_3$. *trans*- β -Phenylhy-

droxylaminemethylenephénylacetic acid (E) was obtained when 10 g. D in ice-cold 50% EtOH was treated with 2–3 g. KOH, warmed 0.5 hr. on a water bath, dild. with H₂O, acidified with dil. H₂SO₄, filtered, dissolved in Na₂CO₃, filtered and acidified and the ppt. recrystd. from 50% EtOH; it is readily sol. in EtOH, fairly sol. in Et₂O or CHCl₃, slightly sol. in petr. ether, insol. in PhH and m. 135°; when D in EtOH is satd. with HCl and allowed to stand overnight, it gives the *ethyl ester*, m. 75°, which yields D on hydrolysis with 20% KOH or F with a more concd. alk. soln. β -Styryl- β -phenylhydroxylamine (F), prepd. by heating E to 160° and recrystg. from EtOH, m. 120°; it is readily sol. in EtOH, CHCl₃ or Et₂O, fairly sol. in petr. ether or PhH and insol. in alkalis. A *di-bromide* (G) of F, obtained when 5 g. F in 20 cc. dry ice-cold CHCl₃ in sunlight is treated with 1.19 cc. Br₂, allowed to stand overnight, and evapd. *in vacuo* at room temp., crystals from CHCl₃ + Et₂O, m. 125°; G in Et₂O or PhH loses HBr on warming, forming a *monobromide* (H), crystals from AcOH or EtOH, m. 179–80°; H with Na in EtOH gives F. α -Cyanostyrylphenylhydroxylamine (J), prepd. by dissolving 20 g. I in 50 cc. AcOH at 70–80°, cooling to 30–40°, adding 15 g. PhNHIOH and recrystg. the ppt. from EtOH, m. 155°, is readily sol. in Et₂O, EtOH or CHCl₃, slightly sol. in PhH or petr. ether and insol. in alkalis; attempts to hydrolyze the CN group or to reduce J were not successful. The following were prepd. in AcOH: *anilinomethylenebenzyl cyanide*, from PhNH₂ and I, crystals from EtOH, m. 150°; *phenylhydrazinomethylenebenzyl cyanide* (K), from PhNHNH₂ and I, crystals from EtOH, m. 155–6°. *Methylenebenzyl cyanide-p-aminophenol*, HOCH₂CH₂NHCH₂CH₂PhCN, prepd. in EtOH, m. 150°, is readily sol. in EtOH or CHCl₃, slightly sol. in Et₂O or petr. ether and insol. in PhH; alk. solns. give yellow crystals of the *sodium* or *potassium salt*; a *copper salt*, prepd. by adding aq. Cu(OAc)₂ to K in EtOH, forms a dark brown powder. N. A. LANGE

Phenyl(trimethylammonium) perhalides. HAMILTON MCCOMBER and T. H. READE. *J. Chem. Soc.* 123, 141–53 (1923).—Since the sulfate and the nitrate do not give stable perhalides, perhalide formation is due to the halogen of the quaternary NH₄ salt and not to the N atom. The bromide gives the widest range of stable perhalides by direct addn. Cl always replaces the N-halogen if I is also present. In the absence of I, Cl replaces the added halogen, not the N-halogen. Br replaces N-I but not N-Cl or added Cl to any appreciable extent. Up to 95° the perhalides have smaller vapor pressures than the parent quaternary NH₄ salts. Low soly. is insufficient to explain these reactions, and the assumption that these perhalides are mol. compds. fails in a similar manner. True chem. affinity where the halogens are multivalent is the only explanation of these expts. These compds. may be degraded by means of CH₂(CO-Et)₂ or Me₂CO. The action of the halogens on a no. of quaternary compds. is described, the following new compds. resulting: *Phenyltrimethylammonium bromide dichloride*, best prepd. by the action of Cl upon PhNMe₃Br₂ in glacial AcOH at 80°, very pale yellow leaflets, m. 111°. I in boiling AcOH gave PhNMe₃Cl₂Cl. The *bromide iodochloride* results from the interaction of ICl and PhNMe₃Br in AcOH and m. 104°. The *bromide iodobromide* results from the action of Br on PhNMe₃BrI₂ or PhNMe₃I₃, by the action of I on PhNMe₃Br₂ or by the action of IBr upon PhNMe₃Br, and forms glistening orange plates, m. 120°. Cl in glacial AcOH gives the *chloride iodotrichloride*, long, yellow needles, m. 144°. The *bromide diiodide* forms deep orange-brown plates, m. 114°. The following solys. in AcOH at 38° are reported: PhNMe₃BrCl₂, 50 g. per l.; PhNMe₃Br₂, 8; NPhMe₂BrI₂, 6.5; PhNMe₃BrIBr, 6.6; PhNMe₃Cl₂Cl, 13.3; PhNMe₃I₃, 4.6. Vapor pressure detns. are given for various perhalides at 33°, 60°, 80°, 89°, 94°, 100° and 155°. C. J. WEST

Catalytic preparation of o-toluidine. C. O. HENKE and O. W. BROWN. *J. Phys. Chem.* 27, 52–64 (1923); cf. C. A. 16, 1403, 1939, 2124.—Ni proved to be too active a catalyst for the reduction of o-MeC₆H₄NO₂ to MeC₆H₄NH₂ with H, as a large part of

the amine was further reduced to the hydrocarbon; the best yield was 86.8%. With a catalyst prepd. from amorphous red lead, a 94.6% yield was obtained. The yield of PhNH_2 from PhNO_2 with the same catalyst was 93.4%. With a fresh Ag catalyst prepd. by reduction of AgCO_3 yields of 99% were obtained, but the activity decreased with use, and an old catalyst gave yields of about 77%. With a Cu catalyst prepd. by reduction of CuNO_3 , 97% of $\text{MeC}_6\text{H}_4\text{NH}_2$ was obtained. When reduced under the same conditions, PhNO_2 gave 91% of PhNH_2 . All of the expts. indicated that *o*- $\text{MeC}_6\text{H}_4\text{NO}_2$ was more easily reduced than PhNO_2 . T. S. CARSWELL

Butyl series. II. The four stereoisomeric β,γ -di-*p*-tolylaminobutanes. G. T. MORGAN AND W. J. HICKINBOTTOM. *J. Chem. Soc.* 123, 97-105(1923); cf. *C. A.* 16, 413.—The condensation of $(\text{MeCHCl})_2$ with *p*- $\text{MeC}_6\text{H}_4\text{NH}_2$ by heating at 130-40° for 30 hrs. gave a mixt. of crude bases which was sepd. by the aid of the HCl salts and picrates. *dl*- β,γ -Di-*p*-tolylaminobutane, purified through the insoly. of its picrate in C_6H_6 , tabular 6-sided crystals, m. 62-3°. *Hydrochloride* (A), hard, nodular crystals with $2\text{H}_2\text{O}$, lost at 100°. *Zinc chloride salt*, white, curdy solid. *Picrate*, orange-red felted crystals, drying to golden yellow, m. 170°. *Benzoate*, prisms, m. 214°. *dl*-Butylene- β,γ -di-*p*-tolylidinitrosodiamine, tabular crystals, m. 88-9°. The *tetrahydroglyoxaline derivative* m. 107-8°; its *picrate* forms clusters of bright yellow needles, m. 137°. *d*-Camphorsulfonate, prismatic needles, m. 222°; no appreciable sepn. of the optically active forms was secured after repeated crystn. The *d*- α -bromocamphor-sulfonate enabled the sepn. into the *d*-form, hard tablets, m. 87-8°, $[\alpha]_D^{20} 100^\circ$. *Hydrochloride*, slender needles. The *l*-form is the more sol. one and forms tablets, m. 87-8°, $[\alpha]_D^{20} -98^\circ$. *Hydrochloride*, slender needles. The *meso*-form, isolated through its HCl salt, is quite insol. in EtOH and forms tabular crystals, m. 57-8°. *Hydrochloride*, prismatic needles, m. 220-30°. *Benzoate*, small crystals, m. 193-4°. The *dinitroso derivative* forms iridescent tablets with a slight buff tint, m. 145-7°, less sol. in MeOH than the *dl*-form. *Tetrahydroglyoxaline derivative*, thin plates or laminas, or needles from EtOH, m. 94°. A by-product of the prepn. of the above butanes is 3,5,7-trimethylacridine (B), isolated by the insoly. of its HCl salt in C_6H_6 , long, pale yellow needles, m. 133-4°. The *hydrochloride* forms felted masses of bright yellow hydrated needles ($3\text{H}_2\text{O}$), which showed intense green fluorescence in dil. aq. soln. *Iodide*, orange-red needles. *Perchlorate*, light yellow; *dichromate*, bulky yellow ppt.; *picrate*, bright yellow powder, m. 225-6°; *nitrate*, small yellow needles. *Methiodide*, slender, scarlet needles. B was synthesized by adding AcH to *p*- $\text{H}_2\text{NC}_6\text{H}_4\text{Me}$, heating until the soln. became darkened, then adding more *p*- $\text{H}_2\text{NC}_6\text{H}_4\text{Me}$ and concd. HCl and heating for 9 hrs. on a sand-bath. By heating A with *p*- $\text{H}_2\text{NC}_6\text{H}_4\text{Me}$ in an open tube at 180-220° for 40 hrs., a small amt. of B was isolated. The yield of B appears to increase with the time of the reaction and with increase in temp. At 180-220° for 40 hrs. the only recognizable products were B and (*p*- MeC_6H_4) $_2\text{NH}$. C. J. WEST

Elimination of the amino group in tertiary amino alcohols. I. ALEX. MCKENZIE AND A. C. RICHARDSON. *J. Chem. Soc.* 123, 79-91(1923).— $\text{H}_2\text{NCHPhCPh}_2\text{OH}$ was prepd. by the action of an excess of PhMgBr upon $\text{H}_2\text{NCHPhCO}_2\text{H}$ or the Et ester. The reaction product from MeMgI would not cryst. and that from $\alpha\text{-C}_{10}\text{H}_7\text{MgBr}$ contained no N and formed lustrous plates, m. 65.5-6.5°. The action of HNO_2 upon $\text{H}_2\text{NCHPhCPh}_2\text{OH}$ invariably gave HOCPhCPh_2 in about 70% yield. The action of HNO_2 upon $\text{H}_2\text{NCHPhCPh}_2\text{MeOH}$ gave ClHMePhCOPh , prisms, m. 59.5-60° (Meyer, *Ber.* 21, 1297, gives 53°). *Semicarbazone*, prismatic needles, m. 161°. $\text{H}_2\text{NCHPhCPh}_2(\text{C}_6\text{H}_5)_2\text{OH}$ gave either naphthyldeoxybenzoin or one of its desmotic isomers, forming rectangular prisms, m. 107-8°. γ -Hydroxy- α,γ,γ -triphenylpropylamine, prismatic needles, m. 146.5-7.5°, and gives a reddish orange color with concd. H_2SO_4 . HNO_2 gives $\text{HOCHPhCH}_2\text{CPh}_2\text{OH}$. *Ethylphenylalanine hydrochloride*, needles, m. 124-5°.

With PhMgBr this yields γ -hydroxy- α,γ,γ -triphenylisopropylamine, glassy needles, m. 144.5–5.5°. HNO_3 gives a compound (probably diphenylmethyl benzyl ketone), rosetts of glassy needles, m. 121.5–2°. Reactions with other tert. NH_2 alcs. are reviewed.

C. J. WEST

The action of alcohols on anilides. ALPHONSE MAILHE. *Bull. soc. chim.* 33, 81–3 (1923).—To det. whether aromatic amides $\text{RCONHC}_6\text{H}_4\text{R}'$, in the same manner as aryl sec. amines, substitute H of the NH group by treatment with alcs., PhNHAc (A) was dissolved in a large excess of warm MeOH, and the soln. in vapor form directed against Al_2O_3 heated to 370–80°; continuous formation of Me_2O took place, and a liquid product condensed which sepd. at once into 2 layers, one being H_2O and unchanged MeOH with a little Me_2O , the second a yellow oil h. 187–200°, consisting of PhNH_2 (B), PhNHMe , and PhNMe_2 ; a residue of unchanged A remained; no exalgin (PhNMeAc) was found; H_2O from MeOH hydrolyzed A, the resulting B being then methylated. A with EtOH or with ProH reacts in a way entirely parallel to the above; in addn., traces resp. of AcH , and of MeAcH and $\text{CH}_3\text{CH:CH}_2$, are formed, but no PhNRAc . Propionanilide, isovaleramide, *o*-acetotoluide, and *o*-benzotoluide all react like A. It appears impossible to alkylate the NH group of aromatic amides by this catalysis.

A. R. ALBRIGHT

Formation of aromatic thiocyanates by the diazonium reaction. A. KORCZYNSKI, J. KNIATOWNA AND F. KAMINSKI. *Bull. soc. chim.* 31, 1179–85 (1922).—Other metallic salts than those of Cu may be used in the prepn. of aromatic SCN compds. A study of the yields of $o\text{-O}_2\text{NC}_6\text{H}_4\text{SCN}$, using the SCN salts of Mn, Cr, Fe, Ni, Co, Zn, Cd, Sn, UO_2 , W and Cu indicates, in comparison with the use of *p*-nitroaniline, that the structure of the compd. affects the ultimate yield, that the yield with the *o*-compd. is better at ordinary temp. than at 60–70°, that $\text{Fe}(\text{SCN})_3$ is the best catalyst (yield 76%), and that W is the next best. $\text{Cu}_2(\text{SCN})_2$ gives a very small yield. Intermediate, definite mol. combinations of the diazonium SCN compd. are described ($m\text{-O}_2\text{NC}_6\text{H}_4\text{SCN})_2\text{Co}(\text{SCN})_2$ is a green cryst. ppt. which decomp. rapidly at 30°. ($m\text{-O}_2\text{NC}_6\text{H}_4\text{SCN})_2\text{UO}_2(\text{SCN})_2$ is a stable solid, decomp. violently by HNO_3 . The Ni compd. is yellow. The W compd. with $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2\text{SCN}$ is brownish and the Mo compd. yellow-orange. The Co double salt with β -diazonaphtbalene is green and decomp. rapidly at 70°, while the Fe salt is brownish red and the Zn salt is yellow. This latter gave a β -naphthalene thiocyanate on decompn.

J. B. BROWN

Azoxyamides and diazo compounds. A. PIERONI. *Gazz. chim. ital.* 52, II, 32–43 (1922).—Phenylazocarboxamide (A) was first obtained by Widman (*Ber.* 28, 1925) and better by Thiele (*Ber.* 28, 2599) by oxidation of PhNHNHCONH_2 with KMnO_4 in neutral soln. (MgSO_4). The MnO_2 and $\text{Mg}(\text{OH})_2$ formed were dissolved with SO_2 . P. obviated the decomp. action of the H_2SO_4 also formed on A by using $(\text{CO}_2\text{H})_2$ instead of SO_2 . Angeli (*C. A.* 12, 364) found that A in KOH gives $\text{PhN:NCO}_2\text{K}$ at first and this PhN:NH (B) and K_2CO_3 . The easy formation of B is also indicated by the ease with which A in alk. soln. gives BzNHNHPh with BzII . A with H_2O_2 gives the azoxy deriv. PhN(O):NCONH_2 (C). According to Angeli (*Gazz. chim. ital.* 46, II, 57) C may have an isomer PhN:N(O)CONH_2 (D), but attempts to obtain both C and D failed. Expts. were then extended to the *p*-bromo- (E) and the *p*-nitrophenylazocarboxamides (F), which could not be obtained by the general method of Widman nor by bromination of A, which gave a mixt. of E and 2,4-dibromophenylazocarboxamide (G) that was difficult to sep. E was best prepd. thus: diazotized $p\text{-BrC}_6\text{H}_4\text{NH}_2$ was treated below 0° with KCNO a little at a time, keeping the soln. feebly acid. $p\text{-BrC}_6\text{H}_4\text{N:NCN}$ (H) sepd. as a yellow ppt. and was sapon. with HCl gas in moist Et_2O , giving E. F was obtained analogously from $p\text{-NO}_2\text{C}_6\text{H}_4\text{N:NCN}$ (I). E, F, G, H and I were all treated with H_2O_2 in AcOH but none of the azoxyamides was obtained in 2 isomeric forms.

The products obtained are considered to be the analogs of C which are not polymerized as was shown by mol. wt. detns. Moreover the constitution of *p*-bromooxy-carboxamide (J) was proved by reducing it to E with Zn and AcOH. J with KBrO in H₂O evolves gas and gives a yellow soln. which when treated with β-naphthol evolves gas and yields red bromophenylazo-β-naphthol. The *p*-nitro-oxy-carboxamide (K) is unstable owing to the NO₂ group which tends to eliminate the azoxy group. K also reacts quickly with alk. β-naphthol, giving *p*-nitrophenylazo-β-naphthol. H and I in AcOH were treated with perhydrol at room temp. (12°) for 40 days after which the AcOH was evapd. spontaneously, giving Br(or NO₂)C₆H₄N(O):NCONH₂. Similar expts. of Bamberger and Baudisch (C. A. 6, 2759) were falsely interpreted and gave *p*-ClC₆H₄N(O):NCN from *p*-ClC₆H₄N:CN. Under similar conditions G does not give the corresponding azoxy deriv. All the azoxyamides here described show analogies to the aromatic diazo compds. J with satd. aq. KOH is slowly converted into the yellow crystals of unstable *potassium p*-bromobenzenesazoxycarboxylate, BrC₆H₄N(O):NCO₂K (of which the free acid was also unknown) and a final product that reacts with β-naphthol. This transformation takes place thus: BrC₆H₄N(O):NCONH₂ → BrC₆H₄N(O):NCO₂H → BrC₆H₄N(O):NH → BrC₆H₄N:NOH. In a large beaker 40 g. KCNO + 10 g. KOH in 100 cc. H₂O were treated with 63 g. KMnO₄ in 1000 cc. H₂O at -17°. After filtering the next day the soln. was added to 50 g. PhNHNH₂ in 100 g. AcOH + 200 cc. H₂O, which gave a white ppt. of phenylsemicarbazide (L). 20 g. L in boiling H₂O and 30 g. MgSO₄ were treated with a slight excess of satd. KMnO₄. The Mg(OH)₂ and MnO₂ were dissolved with dil. (CO₂H)₂ added to the neutral point and A was filtered off. 10 g. powdered A in 210 cc. glacial AcOH were treated with 20 cc. perhydrol. After 25 days the soln. was evapd. spontaneously and sepd. phenylazoxy-carboxamide (C) as long needles, m. 150° (decompn.). 10 g. C in CHCl₃ soln. were treated with 10.7 cc. Br₂ in 30 cc. CHCl₃ at 10° and on evap. deposited G as orange-yellow needles, m. 184°, which could not be oxidized by H₂O₂. 14 g. powdered *p*-BrC₆H₄NH₂ were suspended in 26 cc. concd. HCl to which 7 g. NaNO₂ in H₂O were added as usual. The soln. was filtered, cooled to -10° and treated with 6 g. KCNO in 30 cc. H₂O, which pptd. H, m. 129°, which was filtered off. The wet ppt. in Et₂O treated with HCl gas (NH₄Cl + concd. H₂SO₄) gave E, which, recrystd. from H₂O, m. 175° (decompn.). 7 g. E treated in glacial AcOH with 10 g. perhydrol for 15 days at 40° gave *p*,*p'*-bromooxy-benzene, as yellow needles, m. 172°. The residue from the evapn., crystd. from EtOH and then H₂O, gave J as yellow needles, m. 201° (decompn.). K was obtained similarly as yellow needles, m. 203° (much decompn.)

E. J. WITZEMANN

Aromatic diarsonic acids and their reduction products. II. H. LIEB AND O. WINTERSTEINER. Ber. 56B, 425-33 (1923); cf. C. A. 15, 3634.—*p*-Phenylenediarisine is very easily prepd. by the reduction of the acid with H₃PO₃, effected by heating over a free flame (instead of a sealed tube, as previously reported). In the prepn. of 3,4-O₂N-(H₂N)C₆H₃AsO(OH)₂ (A) there is also formed bis-[3-nitro-4-aminophenyl]arsinic acid, rhombic tables. 2(3)-Nitro-*p*-phenylenediarisonic acid, by the action of Na₂HAsO₄ upon diazotized A in the presence of a little CuSO₄, refractive prisms, decomp. 239-43°. *Sodium salt*, needles. The corresponding *amino acid* is obtained by reduction with Na-Hg in MeOH at 40-50°, the reaction requiring 10-14 hrs. It forms long reddish yellow prisms. With H₃PO₃ this NH₂ acid yields *amino-p*-phenylenediarisine or *diamino-p*-diarsenobenzene, ochre-yellow to brownish red amorphous powder, gradually decomp. at 217-20°. The *hydrochloride* is an amorphous, brick-red ppt., which decomp. above 220°. 2(3)-Methyl-1,4-phenylenediarisonic acid, leaflets, decomp. above 330°. Heated with *magnesia mixt.* it yields a *magnesium salt* as an amorphous ppt. *Tetrasodium salt*, with 9 H₂O. *Acid barium salt*, amorphous. If H₂S is passed through the acid in H₂O on the H₂O bath, the *disulfide* C₆H₃As₂, pale yellow, amorphous ppt., results. The

product of the reaction of H_2PO_3 , heated 3–4 hrs. at 190° , is an orange ppt., *methyl-phenylenediarisine*(?), insol. in all solvents but easily oxidized by HNO_3 or H_2O_2 .

C. J. WEST

The arsenates of aniline. E. PATERNÒ. *Gazz. chim. ital.* 52, II, 28–31(1922).—The arsenate of PhNH_2 (A), $\text{AsO}_4\text{H}_3.2\text{PhNH}_2$, m. 140° , was described by Béchamp. Heated to 180° A loses PhNH_2 , giving $\text{AsO}_4\text{H}_2.\text{PhNH}_2$ (B). P. prepd. A and found that aq. H_3AsO_4 acting on PhNH_2 in any proportions gives the fusible salt A contg. the reagent that was used in excess. Freshly prepd. A is moist but contains no H_2O of crystn. It is best dried over freshly distd. PhNH_2 . The aq. soln. of A when distd. with steam loses nearly all of its PhNH_2 slowly. 50 g. A boiled with 50 g. C_6H_6 loses 8 g. PhNH_2 . Similar results were obtained with Et_2O . A loses PhNH_2 in a desiccator over H_2SO_4 at room temp. A at 60° in *vacuo* loses 1 mol. PhNH_2 , giving B as a rose-gray powder, which gives prisms from EtOH , m. 154° . B under a bell jar with PhNH_2 gives A. The m. p. of A is variable. Mixts. of A and B do not show lowerings of the m. p. but behave as though they were the same compd. in various stages of purity. A is probably so unstable that it decomps. in melting so that its m. p. could not be detd. Mol. wt. detns. in PhNH_2 show that in this solvent B dissociates to give 2 mols. and A to give 3 mols. F. p. detns. on the system $\text{PhNH}_2\text{--H}_2\text{O}$ showed that the max. soly. of PhNH_2 in H_2O at -0.6° is $\pm 3.7\%$ while that of H_2O in PhNH_2 at 5.4° is 2.8% . Alexeiev (*Ber.* 10, 708) found that PhNH_2 is less sol. in H_2O (3.11%) than H_2O in PhNH_2 (4.58%) at room temp. P. found that 3.6% PhNH_2 dissolved in H_2O at temps. not over 30° in 3 mos.

E. J. WITZEMANN

Arsenated benzanilide and its derivatives. W. LEE LEWIS AND C. S. HAMILTON. *J. Am. Chem. Soc.* 45, 757–62(1923).—The arsenated benzanilides below were prepd. from $\text{Cl}_2\text{AsC}_6\text{H}_4\text{COCl}$ and 2 mols. of the aromatic amine in C_6H_6 or xylene, the crude product being converted with H_2O_2 in AcOH into the arsonic acid which with Na halide gave the dihalide and on reduction in the usual way in alc. with H_2PO_3 or H_2PO_2 yielded the arsono deriv. In this way were prepd. *p*-arsono- and *p*-arsono-benzoylanilide, *anthranilide*, *o*- and *p*-aniside and *p*-phenetide. Hydrated *p*-arsonobenzoylarsanilide, $\text{H}_2\text{O}_2\text{AsC}_6\text{H}_4\text{NHCOC}_6\text{H}_4\text{As}(\text{OH})_2$, from $\text{Cl}_2\text{AsC}_6\text{H}_4\text{COCl}$ and $\text{H}_2\text{NC}_6\text{H}_4\text{AsO}_3\text{H}_2$ in NaHCO_3 gives in NaOH with H_2O_2 *p*-arsonobenzoylarsanilide. *p*-Arsenobenzoyl-*p*-xylylide and *o*-*naphthylamide* were also made. *Diiodo-p*-arsinobenzoyl-*p*-aniside, m. $209\text{--}10^\circ$; *p*-phenetide, m. $227\text{--}8^\circ$; *ethylanilide*, m. $115\text{--}6^\circ$; *o*-aniside, m. $148\text{--}9^\circ$. *Dibromo-p*-arsinobenzoyl-*o*-aniside, m. $167\text{--}8^\circ$. *Dichloro-p*-arsinobenzoyl-*o*-aniside, m. $164\text{--}5^\circ$; *ethylanilide*, m. $147\text{--}8^\circ$. *Gluconyl-p*-arsanilic acid, $\text{HOCH}_2[\text{CH}(\text{OH})_4]\text{CONHC}_6\text{H}_4\text{AsO}_3\text{H}_2$, from gluconic acid and $\text{H}_2\text{NC}_6\text{H}_4\text{AsO}_3\text{H}_2$ in MeOH . *3,4*-Digluconylamino-phenylarsonic acid, from $(\text{H}_2\text{N})_2\text{C}_6\text{H}_3\text{AsO}_3\text{H}_2$. C. A. R.

Arsenated benzophenone and its derivatives. II. W. L. LEWIS AND H. C. CHEETHAM. *J. Am. Chem. Soc.* 45, 510–5(1923); cf. *C. A.* 16, 248.—The ultimate aim of this work was the prepn. of a type of arsenical in which the Bz group, with and without solubilizing groups in its nucleus, should replace the HO groups of arspenamine. *o*- $\text{Cl}_2\text{AsC}_6\text{H}_4\text{COCl}$ (A) was successfully prepd., but the reduction of the arsenated nitrobenzophenones to amines and their further reduction to the arsono compds. presented so many obstacles that the attempt was deferred. In the absence of NO_2 or NH_2 groups in the ring, the benzophenonearsonic acids are easily and quant. reduced in AcOH by concd. HBr or HI to derivs. of As_2O_3 and in some cases further to cryst. dibromo- or diiodoarsines, the latter of which are easily converted back into the oxide by hydrolysis with dil. Na_2CO_3 . Likewise, the arsono derivs. of the *o*-arsenated benzophenones are easily formed by refluxing the arsonic acids, or, better still, the arsenious oxides with H_2PO_4 in alc. *o*- $\text{HO}_2\text{CC}_6\text{H}_4\text{AsO}_3\text{H}_2$, prepd. by Bart's method (Ger. pats. 250,264 and

254,345), gives, through *o*-dichloroarsinobenzoyl chloride (A) (prepd. with PCl_5 and then PCl_3 in CHCl_3), with C_6H_6 and AlCl_3 in CS_2 and subsequent treatment with alk. H_2O_2 benzophenone-2'-arsonic acid, softens 105° but does not m. 250° . 4-Methoxybenzophenone-2'-arsonic acid was similarly prepd. with PhMe instead of C_6H_6 , as were also the 4-methoxy, 4-ethoxy and 4-phenoxy analogs. 4,4'-Dibenzoylarsenobenzene was prepd. from $\text{BzC}_6\text{H}_4\text{AsO}$ refluxed in alc. with H_3PO_3 and the 2,2'-dibenzoyl, 2,2'-di-*p*-anisoyl and the 2,2'-di-*p*-ethoxybenzoyl derivatives from the above arsonic acids. 4-Methoxybenzophenone-2'-dibromoarsine, from the arsonic acid in cold AcOH with HBr , m. 161° ; 4-ethoxy homolog, m. 152° . 4-Methoxybenzophenone-2'-arsenious acid, from the dibromide warmed in alc. with dil. Na_2CO_3 , gives on refluxing in AcOH-HCl the 2'-dichloroarsine, m. 148° ; 2'-diiodoarsine, from the arsonic acid in cold AcOH with HI , m. 137° . 4-Ethoxybenzophenone-2'-diiodoarsine, m. 151° . 4-Methoxybenzophenone-4'-dichloroarsine, from the oxide refluxed in AcOH-HCl , m. 152° ; 4'-dibromoarsine, m. 136° ; 4'-diiodoarsine, m. 105° . The dibromoarsine in cold NaOH with $\text{ClCH}_2\text{CO}_2\text{Na}$ gives 4-methoxybenzophenone-4'-arsinoacetic acid, $\text{MeOC}_6\text{H}_4\text{COC}_6\text{H}_4\text{As}(\text{O}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$. $\text{p-H}_2\text{NC}_6\text{H}_4\text{-COMe}$ yields acetophenone-*p*-arsonic acid by the Bart method. C. A. R.

p-Nitrophenylstibinic acid. G. CHARRIER. *Gazz. chim. ital.* 52, II, 16-8 (1922).—*p*-Nitrophenylstibinic acid (A), $\text{p-O}_2\text{NC}_6\text{H}_4\text{SbO}_3 \cdot n\text{H}_2\text{O}$, has been synthesized by the action of diazonium salts on alkali antimonites but is more easily obtained from the addn. compds. of diazonium salts with SbCl_5 . A, like the *o*-deriv. and unlike the *m*-deriv., is insol. in HCl and easily sol. in MeOH and EtOH . 83 g. $\text{p-O}_2\text{NC}_6\text{H}_4\text{N}_2\text{H}_3$ in 150 cc. $\text{H}_2\text{O} + 600$ cc. HCl (d. 1.12) were cooled to 0° and treated with 47 g. NaNH_2 . After filtration the soln. was treated with SbCl_5 from 90 g. Sb_2O_3 in 420 cc. HCl (d. 1.12) at 0° . The pptd. double salt, $\text{p-O}_2\text{NC}_6\text{H}_4\text{N}_2\text{SbCl}_6$, was washed with H_2O and suspended in much H_2O . 10% NaOH was added with cooling until slightly in excess. After standing overnight the soln. was filtered and acidified with HCl . The yellow-brown ppt. (A) was filtered, washed, dried, washed with concd. HCl to remove inorg. Sb compds. and then dissolved in EtOH-HCl . Pure A (probably $[\text{p-O}_2\text{NC}_6\text{H}_4\text{SbO}_3 \cdot 2\text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}$) is a chrome-yellow powder that decomp. about 300° without melting. E. J. WITZEMANN

Mercurization in the aromatic series. II. Thymolmercuric acetates and derivatives. EPISIO MAMELI and ANNA MAMELI-MANNESSIER. *Gazz. chim. ital.* 52, II, 1-16 (1922); cf. C. A. 16, 2681.—In general Hg^{++} salts of OH acids mercurate thymol but as with PhOH the best results are obtained with $\text{Hg}(\text{OAc})_2$, which gives mono- and dimercurated products. The di-deriv. has received the most attention owing to its therapeutic uses. Previous work beginning in 1889 is reviewed. Rupp (C. A. 12, 739) showed that Hydrargyrium thymolaceticum is thymolmercuric diacetate, $1,3,4,2,6\text{-C}_6\text{HMe}(\text{OH})(\text{C}_6\text{H}_7)(\text{HgOAc})_2$ (A) by converting it into 2,4-dinitrothymol. Paolini (C. A. 16, 557) obtained another disubstituted deriv. M. and M. have obtained besides the 2 di-derivs. an *o*-deriv., $1,3,4,2\text{-C}_6\text{H}_2\text{Me}(\text{OH})(\text{C}_6\text{H}_7)\text{OAc}$ (B) and a previously unknown 1,3,4,6-deriv. (C). The position of the HgOAc group was detd. by the action of alkali solns.: both B and C gave the corresponding hydroxides of which that derived from B gave the internal oxide $\text{Me}(\text{C}_6\text{H}_7)\text{C}_6\text{H}_4\text{O.Hg}$ (D) and C gave a compd. $[\text{Me}(\text{HO})(\text{C}_6\text{H}_7)\text{C}_6\text{H}_2\text{HgO}]_2$ (E), as was shown by analysis and mol. wt. detns. In order to confirm the results with C the behavior of the Hg derivs. of PhOH with diazonium salts was studied. Thus *o*- $\text{HO-C}_6\text{H}_4\text{HgCl}$ gives 4,2- $\text{HO}(\text{ClHg})\text{C}_6\text{H}_4\text{N:NPh}$ (F) while *p*- $\text{HO-C}_6\text{H}_4\text{HgCl}$ gives the 2,5-compd. (G). Similarly 2,4- $\text{HO-C}_6\text{H}_4(\text{HgCl})_2$ gives mainly 4,3- $\text{HO}(\text{ClHg})\text{C}_6\text{H}_4\text{N:NPh}$ (H) and some 2,3,5- $\text{HO}(\text{ClHg})_2\text{C}_6\text{H}_3\text{N:NPh}$ (I). With C the HgOAc is substituted, confirming its position as detd., and another N_2Ph reduced, giving 1,3,4,2,6- $\text{C}_6\text{HMe}(\text{OH})(\text{C}_6\text{H}_7)(\text{N:NPh})_2$ (J). In substituting HgOAc with other groups (HgX) the alk. solns. when treated with KCl , KBr , K_2SO_4 , KNO_3 ,

give the corresponding salts of thymolmercury, which by the action of CO_2 give **D** and **E**, resp. Besides being obtained by double decompn., the chlorides corresponding to **B** and **C** were also obtained by treating **B** and **C** directly with NaCl . The ppt. as obtained also contains some 1,3,4,2,6- $\text{C}_6\text{HMe}(\text{OH})(\text{C}_6\text{H}_5)(\text{HgCl})_2$ (**K**), which was also obtained directly from **A**. The yield of **A**, **B** and **C** varies greatly with the nature and quantity of the solvent, the duration of the reaction and the mol. ratio of thymol and $\text{Hg}(\text{OAc})_2$ used. As solvents EtOH and dil. or glacial AcOH or mixts. are best adapted. In the absence of solvents the $\text{Hg}(\text{OAc})_2$ is reduced to metallic Hg . The quant. results of 12 expts. are summarized in a table for which see the original. **B** is much more rapidly converted into **A** with $\text{Hg}(\text{OAc})_2$ than **C**. 31.8 g. $\text{Hg}(\text{OAc})_2$ was agitated with 30 cc. EtOH + 90 cc. AcOH until largely dissolved. 30 g. thymol in satd. alc. soln. were then added. The mixt. was heated at 90° until a white deposit sepd. and was allowed to stand some time. On evapg. the soln. **C** and some **A** sepd. On further evapn. mixts. of **B** (m. $144-5^\circ$) and **C** (m. 188°) sep. These mixts. are fractionated repeatedly and finally freed from **A** by extg. with C_6H_6 in which **A** is insol. On evapn. of the C_6H_6 **C** seps. first. The 3 compds. can also be sepd. by successive extn. with abs. EtOH , 60% EtOH and Me_2CO . *o*-Thymolmercuric acetate (**B**) seps. from C_6H_6 as a finely cryst. powder, m. 147° (182° when heated rapidly in a previously heated bath), is sol. in dil. alkali, giving the corresponding hydroxide, which with CO_2 gives the oxide (**D**). The *p*-isomer (**C**) seps. as small shining crystals, m. 163° , decomp. $178-80^\circ$. The soln. in dil. alkali with CO_2 gave **E**. Neither **B** nor **C** reacts with H_2S . On adding a soln. of **C** and NaOH to PhN_2Cl thymol-2,4-diazobenzene (**J**) was obtained as dark-red long needles, m. 181° , identical with **J** obtained directly from thymol. *o*,*p*-Thymolmercuric diacetate (**A**) m. 218° (bath 200°) is insol. in common solvents except AcOH and unlike **B** and **C** it is insol. in H_2SO_4 . *o*,*p*-Thymolmercuric chloride (like **B**), m. $144-5^\circ$, decomp. 160° , and is best prepd. by adding NaCl to alk. solns. of **B**. *p*-Thymolmercuric chloride was obtained similarly as fine needles, m. 188° , decomp. 195° . **A** in alk. soln. or in aq. suspension pptd. *o*,*p*-thymolmercuric dichloride (**K**), m. $210-1^\circ$, which is insol. in common solvents. *o*-Thymolmercuric bromide ppts. from 5% NaOH solns. of **B** on adding KBr as a cryst. powder, that shrivels at 140° and reddens and sublimes at 180° . *p*-Thymolmercuric bromide is obtained similarly as a white compd. m. 149° (decompn.). **A** filtered soln. of **B** in 5% NaOH with 25% H_2SO_4 ppts. the *o*-thymolmercuric sulfate as a white powder that reddens without melting at 220° . The similar *p*-isomer obtained in the same way decomp. 235° without melting. *o*-Thymolmercuric nitrate was pptd. from NaOH soln. with HNO_3 as a reddish white powder, m. $148-50^\circ$, decomp. 155° . The *p*-isomer was obtained similarly as a white powder, m. 167° (decompn.). **B** treated with 4 mols. of 10% NaOH and then 7-8 vols. hot H_2O , filtered and treated with CO_2 gives *o*-thymolmercuric oxide (**D**), blackens and m. 195° , mol. wt. in PhOH 327, 309, 374 (calcd. 348). **B** heated a long time in C_6H_6 slowly ppts. **D**. **C** treated similarly gives **E** as a heavy white powder that blackens at 180° and decomp. about 205° ; mol. wt. in PhOH 658.8 (calcd. 713.4). *p*-Thymolmercuric hydride sepd. from a 10% NaOH soln. of **C** on standing as a white compd. m. $190-5^\circ$ (decompn.).

III. Mercurated derivatives of *p*-iodothymol. ERISIO MAMELLI. *Ibid* 18-23.—While the mercurization of phenols by Pesci's method (i. e., with $\text{Hg}(\text{OAc})_2$) generally gives dimercurated derivs., *p*-iodothymol (**A**) gives *p*-iodothymolmercury *o*-acetate 1,3,4,6,2- $\text{C}_6\text{HMe}(\text{OH})(\text{C}_6\text{H}_5)(\text{HgOAc})_2$ (**B**), from which the corresponding chloride and bromide were obtained. The HgOAc group was shown to be present in the *o*-position by the fact that the hydrate gives the internal oxide $\text{IMe}(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_2\text{HgO}$ (**C**), which is formed only in

compds. substituted in this way (preceding abstr.). **I** acting on **B** gives various products according to the conditions. In the presence of KI an amorphous iodated product identical with aristol or annidalin (**D**) (a com. disinfectant of unknown consti-

tution) is obtained. The fact that **D** can be obtained in this way is able to confirm 2 of the various hypotheses proposed for its constitution. Compds. **A**, **B** and **C** in the preceding abstr. by the same treatment also give **D**, which is probably a mixt. of 1 derivs. Similar studies on the thymoquinones and their derivs. are under way. 8 g. *p*-iodothy-mol (prepd. by Woollett's method (*C. A.* 15, 1529)), and 2 g. $\text{Hg}(\text{OAc})_2$ in 30 cc. $\text{AcOH} + 90$ cc. EtOH were heated under a condenser for 2 hrs. On cooling there sepd. 7.4 g. **B**, m. 170° , reddens and decomps. at 175° . The aq. suspension of **B** deposits HgS almost at once on adding H_2S . With concd. HCl **B** gives **A**. **B** in 4 mols. dil. NaOH with 1 mol. **I** in 4 mols. KI gives a ppt. of **D**. The 5% NaOH solu. of **B** treated with NaCl ppts. the *chloride* (corresponding to **B**), yellows at 119° , m. $122-4^\circ$. The *bromide* was obtained similarly as a powder that yellows at 102° , m. $105-8^\circ$. **B** in 5% NaOH with CO_2 gives a ppt. of the *internal oxide* (**C**), m. $162-5^\circ$, mol. wt. 479.3 (calcd. 474.6), does not ppt. HgS with H_2S in aq. suspension but does so with $(\text{NH}_4)_2\text{S}$. IV. Di-mercurated derivatives of guaiacol. EFISIO MAMELI. *Ibid* 23-7.—The little known about Hg derivs. of polyphenols and of guaiacol especially is reviewed. In continuing expts. on the mercurization of phenols the action of $\text{Hg}(\text{OAc})_2$ on guaiacol was studied. Mono- and dimercurated derivs. were obtained in various proportions depending on the conditions. In AcOH-EtOH (cf. *C. A.* 16, 2681) more of the di-deriv. was obtained. The mono-derivs. will be described later. That the product was guaiacolmercuric *o,p*-diacetate, $1,2,4,6\text{-C}_6\text{H}_2(\text{OAc})(\text{OMe})(\text{HgOAc})_2$ (**A**), was shown by the fact that with HNO_3 it gives 2,4-dinitroguaiacol (**B**). This behavior corresponds with observations on phenol, thymol, α -naphthol, saligenin, etc. **A** is sol. in NaOH or KOH , giving the *dihydroxide* which is converted into the *internal oxide* $\text{MeO}(\text{HOHg})\text{C}_6\text{H}_3\text{HgO}$ (**C**) with CO_2 . **A**

treated with the corresponding alkali salts gives the *dichloride* as a cryst. powder, browns at $170-80^\circ$ without melting, and the *dinitrate* as an infusible cryst. powder. In the mercurated derivs. of guaiacol the acid group attached to Hg is readily substituted. **A** was best obtained thus: 12.4 g. guaiacol in a little EtOH were dissolved in 63.7 $\text{Hg}(\text{OAc})_2$ in $\text{HOAc} + \text{EtOH}$ (1 : 3) and heated under a condenser for 2 hrs. On slow evapn. **A** seps. first. To purify **A** it was dissolved in NaOH and pptd. with HOAc . On heating **A** yellows, then reddens, but does not m. **A** agitated with 2.5 mols. KNO_3 in 5 times its wt. of glacial AcOH and finally cooled and treated with 1.5 unols. H_2SO_4 gives a liquid, from which after standing some time **B** is pptd. by adding much H_2O . Purified from EtOH , **B** m. $122-3^\circ$. **A** warmed in 5 times its wt. of 5% NaOH and satd. with CO_2 deposited **C** as a heavy ppt. that browns at $200-10^\circ$ but does not m. V. Binary and ternary systems relative to mercurization. E. MAMELI and C. COCCONI. *Ibid* 113-20.—In paper 1 the mercurization of PhOH with $\text{Hg}(\text{OAc})_2$ was studied and *o*- and *p*- $\text{HOC}_6\text{H}_4\text{HgOAc}$, which may be considered the fundamental products in the mercurization of PhOH , were isolated. In further study of the mechanism of mercurization reactions some of the systems involved were studied from the point of view of equil. After a review of the older substitution theory for interpreting this reaction the view of Manchot (*C. A.* 15, 508, 2627) and Kharasch and Jacobsen (*C. A.* 16, 74) that an addn. product is 1st formed in the case of the amines ($\text{PhNH}_2\text{HgX}_2$) which by transposition is mercurated in the ring is discussed. In these cases the direct demonstration of the formation of intermediate products of addn., which could be detd. by the f. p. curve of the system, is lacking. Similar systems have been studied by Mascarelli, *et al.* (*Gazz. chim. ital.* 37, 1, 125(1907); 39, 1, 251(1909)) and found to give addn. products. The 4 systems involved are (1) $\text{PhOH-Hg}(\text{OAc})_2$, (2) $\text{PhOH-Hg}(\text{OAc})_2\text{-AcOH}$; (3) $\text{PhOH-Hg}(\text{OAc})_2\text{-EtOH}$; (4) $\text{PhOH-Hg}(\text{OAc})_2\text{-H}_2\text{O}$. Systems (3) and (4) show limitations due to the phys. consts. of the components, to the decomposability of the $\text{Hg}(\text{OAc})_2$ through the action of heat or the action of EtOH , to the small soly. of $\text{Hg}(\text{OAc})_2$ in H_2O (25% at 10° , 50% at 100°) and EtOH (5.3% at 19° , etc.). The 1st 2 systems show less limi-

tations than the others and are more important from the point of view of practical mercurization since (1) gives the monoacetates and (2) gives the corresponding diacetates. For the study of (2) 3 binary systems: $\text{PhOH-Hg}(\text{OAc})_2$; PhOH-AcOH ; $\text{AcOH-Hg}(\text{OAc})_2$, were required but unknown. For $\text{PhOH-Hg}(\text{OAc})_2$ the f. p. curve corresponds to a sepn. of solid PhOH and shows no product of combination. PhOH-AcOH are miscible in the liquid state, do not combine and show a eutectic at 15.3° . Only the portion of the curve for $\text{AcOH-Hg}(\text{OAc})_2$ corresponding to the sepn. of AcOH was detd. owing to the soly. of $\text{Hg}(\text{OAc})_2$ in AcOH (5.5%). The ternary system (2) could therefore only be developed for solns. rich in PhOH . So far as developed, the series of isotherms obtained show the presence of no product of addn. A similar study of the system $\text{PhNH}_2\text{-(Hg-(OAc)}_2\text{)}$ failed to show an addn. product. The results show that under the conditions of temp. and soly. used $\text{PhOH} + \text{Hg}(\text{OAc})_2$ and $\text{PhNH}_2 + \text{Hg}(\text{OAc})_2$ do not form addn. products. These results must be considered only as a step in the study of the equilibria of this reaction.

E. J. WITZMANN

Oxidation of *o*-toluenesulfonamide. A. V. PAMFILOV. *Bull. Inst. Poly. Ivanovo-Voznesensk* 4, 167-8(1921).—In the oxidation of *o*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{NH}_2$ to *o*-benzoic sulfonide ("saccharin") by means of KMnO_4 , the yield is increased by 10-15% and the proportion of KMnO_4 required diminished by nearly 50% if the alkali salt of the amide is used instead of the free amide. Electrolytic oxidation of the amide (Chem. Fabrik vormals von Heyden, Ger. 85491), like that of *p*- $\text{MeC}_6\text{H}_4\text{SO}_2\text{H}$ (Sebor, *Z. Elektrochem.* 9, 370-3(1903)), gives unsatisfactory results.

J. C. S.

Sulfonic acids. JULIUS V. BRAUN AND WILHELM KAISER. *Ber.* 56B, 549-53 (1923).—In an attempt to prep. compds. of the type $\text{R}_2\text{NCSS.S.O}_2\text{R}'$, that their stability might be compared with compds. of the type $\text{R}(\text{O})\text{C.S.C}(\text{S})\text{NH}_2$, $\text{R}'\text{SO}_2\text{Cl}$ was caused to react with $\text{R}_2\text{NCSSH.NHR}_2$; instead of the expected compd. however, the corresponding $(\text{R}_2\text{NCSS})_2$ was obtained, together with $\text{R}'\text{SO}_2\text{H.NHR}_2$. That is, the sulfonyl chloride simply acted as an oxidizing agent, itself being reduced to the sulfonic acid. 4 mols. Me_2NH , 2 mols. CS_2 and 1 mol. PhSO_2Cl in dry Et_2O gave about 80% of the theory of $(\text{Me}_2\text{NCSS})_2$ and PhSO_3H , isolated through the Fe salt. *Dipiperidylthiuram disulfide* (A), $\text{C}_{17}\text{H}_{29}\text{N}_4\text{S}_4$, obtained in 60% yield, m. 128° . *Tetralin- β -sulfonylpiperidine*, $\text{C}_{16}\text{H}_{11}\text{SO}_2\text{NCC}_6\text{H}_9$, obtained in a small yield (in addn. to a 70% yield of A), from the interaction of $\text{C}_6\text{H}_{11}\text{N}$, CS_2 and $\text{C}_{10}\text{H}_7\text{SO}_2\text{Cl}$, m. $98-100^\circ$. *Tetralin- β -sulfonic acid*, needles from concd. aq. solu., m. $87-8^\circ$. *Benzenesulfonic anilide*, from the chloride and PhNH_2 in dry Et_2O at 0° , m. $112-4^\circ$. Heated with acids, a deep-seated change occurs, without a smooth splitting into the components. The latter takes place by short beating with dil. alc. KOH or upon longer standing in the cold. The *piperidine* sinters at 80° and m. 83° . The *dimethylamide*, yellow oil, b.p. 90° . The *amide*, prepd. in Et_2O with $\text{Et}_2\text{O-NH}_2$, m. 121° . *Toluene-*p*-sulfonic amide*, small needles, m. 120° ; *anilide*, m. 138° .

C. J. WEST

The separation of *m*- and *p*-cresols from coal-tar crude carboic acid. A. F. CAMPBELL. *J. Ind. Eng. Chem.* 14, 732-7(1922).—The fractions obtained by the distn. of the crude product consist principally of (1) PhOH , (2) *o*-cresol, (3) *m*- and *p*-cresols and (4) xylenols and other complex phenols. Fractionation of (3) gives a PhOH -free product contg. 59-60% *m*-cresol. The sulfonation of this with 96% H_2SO_4 at 40° for 6 hrs., and subsequent treatment with H_2O gives an ext. (A) of non-sulfonated cresols and an aq. soln. (B) of monosulfonates contg. 78-80% of the *m*-compd. B is converted into the NH_4 salts through the Ba salts and on fractional crystn. yields a product contg. 98-100% *m*-cresol. The further sulfonation of A with 96% H_2SO_4 gives a non-sulfonated product (C) contg. about 80% *p*-cresol and a sulfonated product (D) contg. about 58% *m*-cresol, which is further sulfonated for obtaining the *m*-compd. C may be treated so that a product contg. 89% *p*-cresol is obtained.

G. W. STRATTON

Addition reactions of the phosphorus halides. VIII. Addition of alkoxy- and aryochlorophosphines to carbonyl compounds. J. B. CONANT, V. H. WALLINGFORD AND S. S. GANDHIKAR. *J. Am. Chem. Soc.* **45**, 762-8(1923); cf. *C. A.* **17**, 544.—In general, P halides of the type APCl_2 and A_2PCl ($\text{A} = \text{R}$ or RO) combine with $\text{C} : \text{O}$ compds. in the same way as PCl_3 . Thus, with BzH in AcOH , PhOPCl_2 , MeOPCl_2 and EtOPCl_2 give AcCl and the oily *phenyl, methyl and ethyl, hydroxybenzylphosphonates*, $\text{PhCH}(\text{OH})\text{PO}(\text{OH})\text{OR}$, and with $\text{PhCH}:\text{CHCOPh}$ PhOPCl_2 yields $\text{BzCH}_2\text{CHPhPO}(\text{OH})\text{OPh}$. *Diphenyl hydroxybenzylphosphonate*, from BzH and $(\text{PhO})_2\text{PCl}$, m. 146° . *Diphenyl α -hydroxyisopropylphosphonate*, from Me_2CO and $(\text{PhO})_2\text{PCl}$, m. $113-4^\circ$; the AcCl produced in its formation reacts with part of it and there is obtained its *acetate*, $\text{Me}_3\text{C}(\text{OAc})\text{PO}(\text{OPh})_2$, m. $72-2.5^\circ$. *Diphenyl α -hydroxy- α -methylpropylphosphonate*, from MeCOEt , m. 128.5° . *Diphenyl α -hydroxy- α -methylbenzylphosphonate*, from MeCOPh , m. 143.5° . *Diphenyl α -hydroxy- α -methyl- β -chloroethylphosphonate*, from $\text{Cl-CH}_2\text{CH}_2\text{COMe}$ and $(\text{PhO})_2\text{PCl}$ in the presence of BzOH (in AcOH the reaction does not take place), m. 119° . $\text{PhCH}:\text{CHCOMe}$ gives $\text{BzCH}_2\text{CHPhPO}(\text{OPh})_2$. The $(\text{PhO})_2\text{PCl}$ was prepd. by heating mixts. of PCl_3 and $\text{P}(\text{OPh})_3$ in sealed tubes; the compns. of the equil. mixts. obtained from mixts. in varying proportions of the 2 reagents are such as would be expected if the 2 reversible reactions $2(\text{PhO})_2\text{P} + \text{PCl}_3 \rightleftharpoons 3(\text{PhO})_2\text{PCl}$ and $(\text{PhO})_2\text{PCl} + \text{PCl}_3 \rightleftharpoons 2\text{PhOPCl}_2$ were involved. C. A. R.

Effect of relative positions of hydroxyl and amino radicals in the migration of acetyl from nitrogen to oxygen. L. C. RAIFORN AND H. A. IDDLIS. *J. Am. Chem. Soc.* **45**, 469-75(1923); cf. *C. A.* **16**, 3472.—It has been found for more than 15 *o*-aminophenols (5 of which have already been reported on) that when both an Ac and a Bz radical are introduced into them the heavier Bz group is found attached to the N , regardless of the order in which the 2 groups were introduced, which shows that in 1 case the Ac radical must have migrated from the N to the O . On the other hand, expts. with a no. of *p*-aminophenols has shown that in these cases no such migration occurs; the occurrence or non-occurrence of a migration of the Ac group from the N to the O when an acetalaminophenol is benzoylated by the Schotten-Baumann method would therefore seem to furnish an additional criterion for distinguishing between *o*- and *p*-aminophenols. *2,6-Dibromo-4-acetylaminophenyl acetate*, from $\text{Br}_2(\text{ClH.H}_2\text{N})\text{C}_6\text{H}_3\text{OH}$ (A) and $\text{Ac}_2\text{O-NaOAc}$, m. $172-3^\circ$; *benzoate* (B), from $\text{Br}_2(\text{AcNH})\text{C}_6\text{H}_3\text{OH}$ (obtained by hydrolysis of the preceding compd.) by the Schotten-Baumann method, m. 168° . *2,6-Br_2(BzNH)C_6H_3OH*, from A, BzCl and NaOH , m. 208° , gives with $\text{Ac}_2\text{O-NaOAc}$ the *acetate*, m. 165° , isomeric, not identical, with B, whose m. p. it depresses to about 153° . *2-Bromo-4-acetylamino-6-methylphenyl benzoate* (C), from $\text{MeBr}(\text{AcNH})\text{C}_6\text{H}_3\text{OH}$ and BzCl , m. 196° . *2-Bromo-4-benzoylamino-6-methylphenol*, from the NH_2 compd., m. 189° , gives with $\text{Ac}_2\text{O-NaOAc}$ the *acetate*, m. 130° , depresses the m. p. of C to 121° . *2,6-Dibromo-4-acetylamino-5-methylphenyl acetate*, from $\text{MeBr}_2(\text{ClH.H}_2\text{N})\text{C}_6\text{HOH}$ and $\text{Ac}_2\text{O-NaOAc}$, m. $145-6^\circ$, hydrolyzed by NaOH to the *4-acetylaminophenol*, m. 222° , which with BzCl in $\text{C}_6\text{H}_5\text{N}$ gives the *benzoate* (D), m. $182-3^\circ$. *2,6-Dibromo-4-benzoylamino-5-methylphenyl acetate*, from the phenol with $\text{Ac}_2\text{O-NaOAc}$, m. 179° , depresses the m. p. of D to 167° . *5,4,6,2-MeBr_2(AcNH)C_6HOH*, from $\text{MeBr}_2(\text{ClH.H}_2\text{N})\text{C}_6\text{HOH}$ and $\text{Ac}_2\text{O-NaOAc}$, m. 216° , hydrolyzed by NaOH to the *2-acetylaminophenol*, m. 171° , which with BzCl-NaOH gives *2-benzoylamino-4,6-dibromo-5-methylphenyl acetate*, m. $195-6^\circ$, identical with the product obtained by acetylation of the *2-benzoylamino-phenol*, m. $198-9^\circ$ (apparent decomposition), which was prepd. from the aminophenol with BzCl in Et_2O . C. A. R.

Acyl derivatives of *o*-aminophenol. R. E. NELSON AND H. L. DAVIS. *Proc. Indiana Acad. Sci.* **1921**, 201-2.—When into *o*- $\text{H}_2\text{NC}_6\text{H}_4\text{OH}$ are introduced the 2 groups RCO- and $\text{RO}_2\text{C-}$, the latter always goes to the N atom regardless of the order of introduction. If RCO- is first substituted on the N atom, when $\text{RO}_2\text{C-}$ is introduced this

is attached to the N atom and RCO- migrates to the O atom. Cf. C. A. 8, 3787; 14, 185; *Am. Chem. J.* 23, 1(1900); 31, 497(1904). A. R. ALDRIGHT

Azoxyphenols. A. ANGELI, DINO BIGIARI, AND GINO CARRARA. *Atti accad. Lincei* 31, (v) i, 439-46(1922).—The difference in behavior towards oxidizing agents shown by isomeric azoxyphenols (C. A. 15, 2278) resembles that observed in the action of halogens or HNO₃ on their isomeric monosubstituted derivs. Thus, of the two *p*-comps., O:NPh:NC₆H₄Br and NPh:NO.C₆H₄Br, only the latter readily yields the further *p*-substituted compds., BrC₆H₄N:NOC₆H₄Br and O₂NC₆H₄N:NOC₆H₄Br, the former resisting the action of Br or HNO₃. Hence the O atom of the azoxy group protects the aromatic nucleus united to the N atom carrying the O from the action, not only of halogens or HNO₃, but also of KMnO₄. Further, this protective action is exercised against HNO₃ in cold, dil. soln.; in this case, one of the isomeric azoxyphenols remains unaltered, whereas the other, instead of being destroyed, is transformed into a nitro deriv., usually easy to characterize, the structure of the original compd. being thus established. Azobenzene, azoxybenzene, *p*, α -azoxyphenol Et ether, *p*, β -azoxyphenol, and *p*-nitrophenol are not changed when excess of NaNO₂ is gradually added to their glacial AcOH solns., while *p*-HOC₆H₄N:NPh, (*p*-HOC₆H₄N:)₂, *p*, α -azoxyphenol, and *p*,*p'*-dihydroxyazoxybenzene, under the same conditions, readily yield nitro derivs. in which the nitro groups occupy *o*-positions with respect to the hydroxyl. For this reaction to occur, it is not sufficient that the aromatic ring contain a HO group, it being necessary also that the hydroxylated nucleus be attached to a tervalent N atom. In the action of HNO₃ on (*p*-HOC₆H₄N:)₂, the dinitro deriv. formed is accompanied by *p*-nitrophenol, the reagent acting partly as an oxidizing agent; this oxidation is completely analogous to that of H₂N₂O₂ by KMnO₄ when the latter acts first in an alk., and subsequently in an acid solution. [3,4-O₂N(HO)C₆H₂N:]₂, obtained from (*p*-HOC₆H₄N:)₂, forms lustrous, greenish yellow needles, m. 236° (decompn.), and is probably identical with the compd., m. 240°, obtained by Robertson (C. A. 7, 3751) by treating (*p*-HOC₆H₄N:)₂ in AcOH with concd. HNO₃. 3-Nitro-4-hydroxyazoxyphenol, O:NPh:NC₆H₄(NO₂)OH, obtained from *p*, α -azoxyphenol, forms transparent, greenish yellow, rhombohedral plates or green, straw-like crystals, m. 125°. 3-Nitro-4,4'-dihydroxyazoxybenzene, HOC₆H₄NO:NC₆H₃(NO₂)OH, prep'd from (*p*-HOC₆H₄N:)₂, forms lustrous, reddish yellow needles or red, straw-like crystals, m. 193° (decompn.). J. C. S.

Rings through the *m*- and *p*-positions of benzene. A study of certain ethers of resorcinol and *m*-aminophenol. W. C. WILSON WITH ROGER ADAMS. *J. Am. Chem. Soc.* 45, 528-40(1923).—Attempts to close *m*- and *p*-rings, starting from various types of phenol ethers, were unsuccessful. Resorcinol bis- β -bromoeethyl ether, from C₆H₄(ONa)₂ and (CH₂Br)₂ in alc., m. 94.5-5.0°, b_p 166-7°. Bis- γ -bromopropyl ether, from C₆H₄(OH)₂, CH₂(CH₂Br)₂ and K₂CO₃ in Me₂CO-H₂O, m. 67°, b_p 204-6°; with C₆H₄(ONa)₂ there are formed, in addn., 3 other products: the γ -bromopropyl allyl ether, C₆H₄(OCH₂-CH₂-CH₂)OCH₂CH₂CH₂Br, m. 88-9°, γ -propyloxyphenyl(allyloxyphenyl)trimethylene-glycol, m. 119-20°, and resorcinol diallyl ether, b₁₂ 156-8°, d₂₀²⁰ 1.1645, n_D²⁰ 1.5672. Bis- γ -iodopropyl ether, from the Br compd. in aq. Me₂CO with NaI, m. 88-9°, is partly converted by Na in Et₂O into the dipropyl ether, also obtained from C₆H₄(OH)₂, PrBr and K₂CO₃ in Me₂CO, b₁₂ 127-8°, d₂₁²⁰ 1.035, n_D³³ 1.5133. Bis- γ -amylaminopropyl ether, from C₆H₄(OCH₂CH₂CH₂)₂ and AmNH₂ heated alone or in PhMe, b₁₀ 249-52°; dihydrochloride, m. 287°. Bis- γ -cyanopropyl ether, from the I compd. and NaCN in aq. alc., b_p 236-7°, m. 31-2°, converted by Na in alc. into the bis- δ -aminobutyl ether, b₁ 208-9° d₂₀²⁰ 1.0589, n_D²⁶ 1.5315, whose dihydrochloride m. 248-9° and mono-hydrochloride m. 233-4°; the latter, distd. under 7 mm., decomp. into pyrrolidine, *m*-C₆H₄(OH)₂ and resorcinol mono- δ -aminobutyl ether, b_p 198-204°, m.

119-9.5° (hydrochloride, m. 159-61°), which in NaOH with $p\text{-O}_2\text{NC}_6\text{H}_4\text{COCl}$ gives *resorcinol mono-6-p-nitrobenzoylaminoethyl ether p-nitrobenzoate*, m. 123-4°. *m-Nitrophenyl γ -bromopropyl ether*, from $\text{O}_2\text{NC}_6\text{H}_4\text{OH}$, $\text{CH}_3(\text{CH}_2\text{Br})_2$ and Na in alc., b₇ 186-8°, d_{20}^{20} 1.513, n_D^{25} 1.5700, reduced by $\text{SnCl}_2\text{-HCl}$ to the *m-amino compound*, unstable yellow oil (hydrochloride, m. 114-5°), which, refluxed in C_6H_6 , gives *6-aminochroman*, b₇ 140-2°, d_{20}^{20} 1.1549, n_D^{25} 1.5944; hydrochloride, begins to decomp. 134°, m. 158-60°; picrate darkens 156-60°, m. 182-3°; chloroplatinate, m. 224-5°, decomps. 227°; benzenesulfonyl derivative, m. 148-8.5°. The diazotized chroman couples with β -naphthol to a red substance, $\text{C}_{10}\text{H}_{10}\text{O}_2\text{N}_2$. *m-Nitrophenyl allyl ether*, from $\text{O}_2\text{NC}_6\text{H}_4\text{OH}$, $\text{CH}_2=\text{CHCH}_2\text{Br}$ and Na in alc., b₃ 136-7°, m. 31.5-2.0°; *m-amino compound*, b₃ 120-2°, d_{20}^{20} 1.0891, n_D^{25} 1.5708; hydrochloride, m. 145-6°; benzenesulfonyl derivative, m. 83-3.5°. *p-Nitrophenol β -bromoethyl ether*, from $\text{O}_2\text{NC}_6\text{H}_4\text{ONa}$ and $(\text{CH}_2\text{Br})_2$ in H_2O , m. 64°; *p-amino compound*, m. 84°; hydrochloride, m. 196°. C. A. R.

Ethylene and trimethylene ethers of dihydroxybenzenes. I. MORITZ KOHN AND FRANZ WILHELM. *Monatsh.* 43, 545-55(1923).—*Bisresorcinol ethylene ether* is easily prep'd. by boiling 80 g. $\text{C}_6\text{H}_4(\text{OH})_2$ and 24 g. $\text{C}_2\text{H}_4\text{Br}_2$ with 10 g. H_2O , adding in small portions 10 g. KOH in 10 g. H_2O . The excess of $\text{C}_6\text{H}_4(\text{OH})_2$ is necessary to avoid oily reaction products. The ether forms thin, strongly refracting needles, m. 163°. *Methyl ether*, by the action of KOH and Me_2SO_4 , or by condensing $\text{C}_6\text{H}_4\text{Br}_2$ with $\text{MeOC}_6\text{H}_4\text{OH}$ by means of EtONa , m. 63°. *Benzoate*, m. 115-6°. In the same way, using $(\text{CH}_2)_3\text{Br}_2$, *bisresorcinol trimethylene ether* is obtained as long flat needles, thin leaflets or short thick prisms, m. 118°. *Methyl ether*, m. 41°. *Benzoate*, thin needles, m. 97-8°. *Bishydroquinol ethylene ether benzoate*, m. 186°. *Methyl ether*, m. 148-50°. The *trimethylene ether* forms rectangular leaflets, m. 142-4°. *Benzoate*, flat needles, m. 138-9°. *Methyl ether*, leaflets, m. 84-5°. *m-C}_6\text{H}_4(\text{OH})_2 and $\text{C}_2\text{H}_4\text{Br}_2$ give a cyclic ether (Vorländer, *Ann.* 280, 201). *Biscatechol trimethylene ether*, thin flat needles, m. 123-5°. The Me ether is identical with that prep'd. by Gattermann (*C. A.* 2, 820). *Benzoate*, m. 91-3°. II. M. KOHN AND LEOPOLD SAFRIN. *Ibid* 557-66.—The action of KOH upon a mixt. of $m\text{-C}_6\text{H}_4(\text{OH})_2$ and $\text{PhOCH}_2\text{CH}_2\text{Br}$ yields *phenyl-m-hydroxyphenyl ethylene ether (A)*, $m\text{-HOC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{OPh}$, m. 86.5°. Me_2SO_4 gives the *methyl ether*, long needles, m. 86-7°, also obtained by condensing $\text{HOC}_6\text{H}_4\text{OMe}$ and $\text{PhOCH}_2\text{CH}_2\text{Br}$ with EtONa . *Benzoate*, prisms, m. 60-1°. The action of a 2nd mol. of $\text{PhOCH}_2\text{CH}_2\text{Br}$ upon A gives *catechol bisethylenebisphenyl ether*, $\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2\text{OPh})_2$ leaflets, m. 116-7°. With $\text{C}_2\text{H}_4\text{Br}_2$ and EtONa , A yields the *bisethylenebisphenyl ether of biscatechol ethylene ether*, $(\text{PhOCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{OCH}_2)_2$, thin, short needles, m. 106-7°, while with $(\text{CH}_2)_3\text{Br}_2$ the same ether of *biscatechol trimethylene ether*, needles, m. 91°, is obtained. *Phenyl-o-hydroxyphenyl trimethylene ether*, transparent prisms, m. 56-7°. *Methyl ether*, prisms, m. 55-6°. *Benzoate*, needles, m. 60-1°. *Catechol bistrimethylenebisphenyl ether*, $\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2\text{CH}_2\text{OPh})_2$, needles, m. 51°. *Catechol ethylenepheryl ether trimethylenepheryl ether*, $\text{PhOCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{CH}_2\text{OPh}$, prisms, m. 66.5-7.5°. *Catechol ethylene ether bistrimethylenebisphenyl ether*, $(\text{PhOCH}_2\text{CH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{OCH}_2)_2$, needles, m. 102-3°. *Catechol trimethylene ether bistrimethylenebisphenyl ether*, needles, m. 61-2°. C. J. WEST*

Synthesis of substituted thianthrenes. I. Thianthrene and nitrothianthrene. SRI KRISHNA. *J. Chem. Soc.* 123, 156-60(1923).—*6-Chloro-3-nitrobenzenesulfinic acid* results by the reduction of the sulfonyl chloride with Na_2SO_3 at room temp. and forms shining plates, m. 139°. Condensed with PhSH in NaOH, it yields *4-nitro-2-sulfenodiphenyl sulfide (A)*, small, lemon-yellow needles, m. 135°. From this *3-nitrothianthrene (B)*, small orange needles, m. 128°, results on standing at room temp. with concd. H_2SO_4 ; it can be dist'd. in a vacuum at 260° and sublimes in long slender orange needles. The concd. H_2SO_4 soln. is deep violet. *3-Aminothianthrene*, needles, m. 185°. *Hydrochloride; sulfate*. The diazotized salts give bright red ppts. with $\beta\text{-C}_6\text{H}_4\text{OH}$.

Addn. of NaNO_3 to a soln. of the NH_2 compd. in $\text{EtOH-H}_2\text{SO}_4$ gave thianthrene. If A is dissolved in concd. H_2SO_4 at 50° , 3-nitrothianthrene monoxide is formed, nodules, m. 166° . HBr in AcOH reduces it to B. Oxidation of B in boiling AcOH with HNO_3 gave the dioxide, $\text{O}_2\text{NC}_6\text{H}_3(\text{SO})_2\text{C}_6\text{H}_4$, light brown prisms, m. 226° . CrO_3 in AcOH gives the tetroxide, $\text{O}_4\text{NC}_6\text{H}_3(\text{SO}_2)_2\text{C}_6\text{H}_4$, prisms, m. 255° . B forms a ferrichloride, dark brown, m. 223° . A dichloride is formed when dry Cl_2 is passed into B in AcOH but it cannot be isolated as moisture converts it into a sulfide. C. J. WEST

Halogenation. XXII. Action of bromine and nitric acid on organic compounds. Preparation of nitrosyl tribromide and the formation of tetrabromoquinone. R. L. DATTA AND N. R. CHATTERJEE. *J. Am. Chem. Soc.* 45, 480-2(1923); cf. *C. A.* 16, 2845.—Just as CCl_3NO_2 and $\text{O}:\text{CCl}_2:\text{O}$ are formed by the exhaustive action of aqua regia on org. compds., so Br and HNO_3 give $\text{O}:\text{C}_2\text{Br}_4:\text{O}$ (A) and a mixt. of bromonitro derivs. of CH_4 . A mixt. of HNO_3 and HBr gives the same results but in this case nitrosyl tribromide is first formed as a dark red oil. Varying amts. of A were obtained in this way from $p\text{-C}_6\text{H}_4(\text{OH})_2$, $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$, $p\text{-H}_2\text{NC}_6\text{H}_4\text{OH}$, PhNH_2 , aniline black, PhNHNH_2 , $p\text{-O}_2\text{NC}_6\text{H}_4\text{OH}$ and $p\text{-H}_2\text{NC}_6\text{H}_4\text{NHNH}_2$, while $m\text{-C}_6\text{H}_4(\text{OH})_2$, $\alpha\text{-C}_{10}\text{H}_7\text{OH}$, $\text{C}_6\text{H}_5(\text{CO})_2\text{O}$, $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$, $m\text{-}$ and $p\text{-MeC}_6\text{H}_4\text{OH}$, mesitylene, cymene, styrene, C_{10}H_8 , anthracene, Me_2CO , EtOH , MeOH , Et_2O , allyl alc. and hexamethylenetetramine gave only inixts. of bromonitromethanes. C. A. R.

Reaction between aniline and chloroacetic acid. I. RYUZABURO NONZU AND SHIGERU KOMATSU. *Mem. Coll. Sci. Kyoto Imp. Univ.* 6, 73-6(1922).—Phenyliminodiacetic acid monoanilide (A), m. 212° , was obtained from 1.04 mol. PhNH_2 and 1 mol. $\text{CH}_2\text{ClCO}_2\text{H}$ by heating on a H_2O bath in a pressure bottle for 1 hr., treating the product with H_2O , digesting with concd. $(\text{NH}_4)_2\text{CO}_3$ and pptg. with HCl . After the removal of unchanged PhNH_2 from this filtrate extn. with Et_2O gave phenyliminodiacetic acid (B), and crystals of $\text{PhNHCHCl}_2\text{CO}_2\text{H}$ (C) from the soln. The residue insol. in $(\text{NH}_4)_2\text{CO}_3$ on extn. with 94% alc. gave in the ext. $\text{CH}_2\text{ClCONHPh}$ (D) and diphenyldiketopiperazine (E) in the residue. The reactions consist in dehydration for the formation of D and removal of HCl for the formation of C. The formation of D is accelerated by HCl , and PhNH_2 accelerates the formation of C. PhNH_2 also accelerates the formation of B from C and $\text{CH}_2\text{ClCO}_2\text{H}$, of E from D and of A from D and C. G. W. S.

Some salts of p -, o - and m -quinonoid structure. III, IV. R. CIUSA AND G. RASSELLI. *Gazz. chim. ital.* 52, II, 121-5, 126-8(1922).—This is a continuation of a former paper on this subject (*C. A.* 14, 3231). The optical study of p - and o -nitrophenylhydrazones and their alkali salts was completed. Data on the m -derivs. will be published next. Besides o - and $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHN}:\text{CHPh}$ (A and B) and their alkali salts the corresponding derivs. of AcCO_2H and their mono- and dimetallic salts were studied. Pyruvic acid p -nitrophenylhydrazone (C), needles, m. 220° , gives a monosodium salt (D), $p\text{-O}_2\text{NC}_6\text{H}_4\text{NHN}:\text{CMeCO}_2\text{Na}$, as yellow scales from AmOH . The monopotassium salt resembles it. C in dry COMe_2 treated with NaOH in abs. EtOH ppts. D at first which then becomes the disodium salt, $p\text{-NaO}_2\text{N}:\text{C}_6\text{H}_4\text{N}:\text{N}:\text{CMeCO}_2\text{Na}$, violet crystals, little sol. in EtOH and MeOH . The dipotassium salt resembles it. Pyruvic acid o -nitrophenylhydrazone (E), yellow needles, m. 221° , gives alkali salts by the methods used with C: monosodium salt, yellow scales; monopotassium salt, yellow scales; disodium and dipotassium salts, yellow with blue metallic reflex. All the alkali salts hydrolyze to the original hydrazones. Results of the spectrographic study (cf. original for graphs) show that the quinonitronic salts are quite stable under the conditions used and obey Beer's law sufficiently. The salt formation with A and B is accompanied by a sharp change due to passing from the benzenoid to the p -quinonoid structure for which the characteristic band at 2100 is evident. C and E and their alkali salts behave quite differently but the 2 series of compds. show similar absorption curves. In the absorption curve of the o -quinone-

nitronic form there is a characteristic band at 2016-2034. This band is displaced to the left with respect to that of *p*-quinone. In the hopes of obtaining a quinonoid Me ester of B, it and its K salt were treated with MeI. A *N*-Me ether was obtained instead. The product showed an absorption spectrum quite similar to that of B and on hydrolysis gave $p\text{-O}_2\text{NC}_6\text{H}_4\text{NMeNH}_2$ (F). This fact does not contradict the quinonoid structure assigned to this compd. by C. Charrier (*C. A.* 10, 1172), by nitrating anthraquinone methylphenylhydrazone and subsequent hydrolysis, obtained a hase m. 142°. F m. 156°, reduces Fehling and $\text{Ag}_2\text{O-NH}_3$ soln., giving a mirror, and condenses with aldehydes and ketones giving the hydrazones. 5 g. of the K salt of B with 40 g. xylene (dried with Na) and 8 g. MeI were heated under a condenser until the ppt. became white (KI). On cooling the *N*-methyl ether (G), $\text{O}_2\text{NC}_6\text{H}_4\text{NMeNHPH}$, seps. as orange-yellow tablets, m. 134°, stable and sol. in org. solvents. Near the m. p. it is converted into a red form which seps. from EtOH as canary-yellow crystals, m. 131°. The orange form is a mixt. (cf. Ciusa, and Vecchiotti, *C. A.* 5, 3405). 5 g. G were suspended in 50 cc. concd. HCl and treated with steam. On dilg. with an equal vol. of H_2O the soln. was satd. with AcONa by which F was pptd. in yellow-brown needles, m. 156°. With BzH F gives G. With AcCO_2H F gives pyruvic acid *p*-nitro-*N*-methylphenylhydrazone as pale orange and red crystals, m. 153°. Satd. aq. F and picric acid ppt. the *picrate*, $\text{O}_2\text{NC}_6\text{H}_4\text{NMeNH}_2\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, m. 131°. F in H_2O treated with concd. FeCl_3 pptd. the *tetrazone* of F which will be studied later.

E. J. WITZEMANN

Possibility of variable intermediate stages in the Kolbe reaction and a case of anodic ester formation with aromatic acids. C. SCHALL. *Z. Elektrochem.* 28, 506-11 (1922).—During the electrolysis of molten $\text{Pb}(\text{OAc})_2$ the following reaction takes place at the anode. $\text{Ph}(\text{OAc})_4 = \text{Ph}(\text{OAc})_2 + \text{C}_2\text{H}_4 + 2\text{CO}_2$. With $\text{Mn}(\text{OBz})_2$ in molten BzOH there takes place at the anode the electrolytic reaction: $\text{Mn}(\text{OBz})_2 + \text{BzO}^- \rightarrow \text{Mn}(\text{OBz})_4$, which is accompanied by the thermal decomp., $\text{Mn}(\text{OBz})_4 = \text{Mn}(\text{OBz})_2 + \text{Ph}_2 + 2\text{CO}_2$. Since such reactions could not be expected with mono- CO_2H acids and bases of const. valence, the above cases suggest the possibility of variable intermediate stages in the Kolbe reaction. BzOPh was obtained at the anode by electrolyzing a 10% soln. of AgOBz in molten BzOH between a Ag anode (22 cm.²) and a Pt-Ag cathode. The yield was about 0.1 g. per amp.-hr. Part of the acid is first oxidized to PhOH by means of Ag_2O formed at the anode, and this is subsequently esterified.

H. JERMAIN CREIGHTON

Production and reactions of 2-dithiobenzoyl. MARY MCKIBBEN and E. W. McCLELLAND. *J. Chem. Soc.* 123, 170-3 (1923).—2-Dithiobenzoyl (A) (*C. A.* 16, 1226) may also be prepd. by the interaction of $\text{HO}_2\text{CC}_6\text{H}_4\text{S}_2\text{H}$ and EtHS or $\text{HSCH}_2\text{CO}_2\text{H}$ in the presence of H_2SO_4 , finally heating to 50° for 2 hrs. $\text{C}_6\text{H}_5\text{NMe}_2$, $\text{C}_6\text{H}_5\text{N}$ and $\text{C}_6\text{H}_7\text{N}$ do not react with A. NH_3 gives 2-thiobenzimide, long needles, m. 158°. Alc. FeCl_3 gives a purple color and on diln. this soln. deposits a blue powder and the original imide. On oxidation it yields saccharin.

C. J. WEST

The reaction of organomagnesium compounds on nitriles. Action of magnesium methyl bromide on phenylacetonitrile. ALB. RONDOU. *Bull. soc. chim. Belg.* 31, 231-41 (1922).— MeMgBr acts in an analogous manner to metallic Na on the nitrile, producing new substances from it by polymerization. Two of these have been obtained pure and examd. The chief product is a himol. polymeride, previously obtained by von Meyer [*J. prakt. Chem.* (2) 62, 81-117 (1895)] as an oil, but now as crystals, m. 114.5-5°. It is stated that crystn. is hindered by traces of impurities. The termol. polymeride differs from those previously prepd., and an attempt to investigate its structure leads to the conclusion that it is 4,6-diamino-3,5-diphenyl-2-benzylpyridine (cf. Wedekind, *C. A.* 5, 1273).

J. C. S.

Decomposition of the aminobenzoic acids by boiling water. L. McMASTER AND

R. L. SHRINER. *J. Am. Chem. Soc.* **45**, 751-3 (1923).—*o*- and *p*-H₂NC₆H₄CO₂H are decompd. by boiling H₂O into PhNH₂ and CO₂ and they are slightly volatile with steam while the *m*-acid neither is decompd. nor volatilizes with steam. The decompn. of the *o*- and *p*-acids is a monomol. reaction, the consts. (time in hrs.) being 0.028-0.033 and 0.018-0.017, resp.

C. A. R.

E. Fischer's acyl-wandering in phenolcarboxylic acids. Synthesis of *p*-di- β -resorcylic acid and *p*-benzoylpyrogallolcarboxylic acid. EUGEN PASCU. *Ber.* **56B**, 407-24 (1923); cf. Fischer, *C. A.* **12**, 1968.—Since in the attempt to prep. *p*-digallic acid the *m*-acid resulted because of the wandering of the galloyl group to the *m*-OH group, it is necessary to prove the constitution of di- β -resorcylic acid by direct synthesis. Proof is offered that in this type of compd., there is no wandering of the aromatic acyl group. 2,4-Diacetyl- β -resorcytyl chloride, from the acid and PCl₅ or SOCl₂, b₁₂ 170° (some decompn.), solidifies at -20°. Anilide, fine, glistening needles, m. 126-7°. Condensation of the chloride with 2-acetyl- β -resorcylic acid at -15° in AcMc-NaOH gave triacetyl-*p*-di- β -resorcylic acid, small prisms, sinter 146°, m. 151-3°. Sapon. with NaOH or 5 N NH₄OH gave *p*-di- β -resorcylic acid, prismatic microneedles, decomp. 211° (cor.). The MeOH soln. gives a red-violet color with FeCl₃. Ac₂O regenerated the tri-Ac deriv. CH₃N₃ gave the methyl ester of the *q*'-methyl ether, fine glistening needles, m. 144-5°. A large excess of CH₃N₃ gives a more highly methylated product, which was not investigated. Methyl 2-acetyl-4-benzoyl- β -resorcyate, hexagonal prisms, m. 99-100°. The action of 1.5 N NH₄OH leads to the splitting off of both the Ac and Bz groups, giving methyl β -resorcyate, needles, m. 121-2°. These and other facts point to the supposition that the acyl wandering is not dependent upon the *o*-position of the phenolic HO group but upon a directive action of the CO₂H group. This view seems to be supported by the behavior of pyrogallolcarboxylic acid. Triacetylpyrogallolcarboxylic acid, by the action of Ac₂O and ZnCl₂ upon the acid, prisms, m. 164°. The action of 2 N NaOH upon the Ac deriv. in KHCO₃ gives the 2,3-diacetyl derivative, long needles, contg. 1 H₂O, quickly lost at 80° and 1 mm., m. 157°. The dil. alc. soln. gives a dark red color with FeCl₃. On crystn. from hot H₂O a partial sapon. occurs, probably forming the 2-acetyl derivative, m. 192°. The methyl ester 4-methyl ether of the diacetate forms rhombic plates, m. 108°. Sapon. gave the MeO(HO)₂C₆H₂CO₂H (*Monatsh.* **25**, 506). The 4-benzoate of the diacetate forms fine needles, m. 161-2°; sapon. with HCl gives 4-benzoylpyrogallolcarboxylic acid, large, glistening leaflets, decomp. 210-11°. Ac₂O regenerates the diacetate. The methyl ester of the 2,3-dimethyl ether forms compact crystals, m. 79-80°, and yields upon hydrolysis with NaOH 2,3-dimethoxy-*p*-pyrogallolcarboxylic acid, rhombic microplates, m. 154-5° and giving a brownish yellow color with FeCl₃.

C. J. WEST

Tannins. II. Chinese tannin. P. KARRER, H. R. SALOMON AND J. PEYER. *Helvetica Chim. Acta* **6**, 3-37 (1923); cf. *C. A.* **16**, 1755.—By a careful fractional pptn. with Al(OH)₃ (A) it is possible to sep. Chinese tannin (B) into fractions which are characterized by differences in optical rotation in H₂O or org. solvents, and which show differences in their pptn. with A. The fractions with a high sp. rotation when treated at room temp. with AcOH-HBr yield tetra[triacetylgalloyl]-1-bromoglucose (C) which is identical with that similarly obtained from synthetic penta[triacetylgalloyl]glucose (D); the two samples of tetra[triacetylgalloyl]-1-acetylglucose (E) and the two samples of tetra[triacetylgalloyl]methylglucoside (F) from both sources, resp., are identical. It is concluded that the tannin fractions with a high $[\alpha]$ value are derived from pentagalloylglucose and that the individual fractions differ from each other in the no. or arrangement of the depside gallic acid linkings, or in the configuration about the 1-C atom of glucose; fractions with a low $[\alpha]$ value as well as the unfractionated B give preps. of C and E which differ from the analogous compds. obtained from D, the difference

probably being caused by naturally occurring impurities. The yields of **E** from high $[\alpha]$ value fractions indicate 8-9 mols. gallic acid (**H**) per mol. sugar; the low $[\alpha]$ value fractions probably contain more depside gallic acid as well as impurities. It is concluded that **B** is a mixt. of many compds. of similar constitution which are galloylated glucoses; this mixt. of similar components causes the amorphous character and the colloid soln. of **B**, as pure individuals would be very slightly sol. in H_2O but the mixt. with impurities forms a supersatd. colloid-like soln. **A** was precipd. by adding slowly with stirring sufficient NH_4OH to ppt. all of the $Al_2(SO_4)_3 \cdot 18H_2O$ (**G**) in a 10% soln. without the latter becoming alk. When 250 g. **B** in 1 l. H_2O is stirred and treated with **A** from 20 g. **G** suspended in H_2O , the soln. remains clear; further addn. of **A** (10 g. **G**) caused a ppt. to form which was stirred 2 hrs. and then placed on ice for 2-12 hrs.; the ppt. was removed and the operation repeated on the filtrate to obtain 5 fractions. Each of the ppts. was treated with sufficient dil. H_2SO_4 to liberate the tannin which was extd. with $EtOAc$, washed with H_2O , dried and evapd. *in vacuo*. Fractions 1 and 2 were dissolved separately in 10 parts H_2O and the solns. placed in an ice box overnight, when a ppt. of salve-like consistency sepd. which is removed and redissolved in H_2O and the cooling repeated to obtain a second pptn.; the supernatant portions are evapd. *in vacuo* and the ppts. dried *in vacuo*; in this manner fractions 1a, 1b, 2a and 2b were obtained. Fraction 1a was sepd. into 3 parts by pptn. with **A**. The sp. rotation of small portions of each fraction in H_2O was detd. and those with values nearly the same were united. After 80 such fractionations, 250 g. **B** was divided as follows (2nd value = $[\alpha]$): 13 g., 30° ; 22 g., 54° ; 33 g., 70° ; 17 g., 80° ; 15 g., 108° ; 8 g., 138° ; 9 g., 147° ; 2 g., 157° . Each fraction was sol. in $EtOH$, Me_2CO , C_2H_5N or H_2O , slightly sol. in Et_2O and insol. in $CHCl_3$; several of the smaller fractions of 1-1.5 g. were not completely sol. in H_2O , which seems to indicate that a pure compd. was at hand since cryst. compds. of the tannin type are insol. in H_2O ; the acidity of each fraction was equiv. to 6.-6.5 cc. 0.1 N per 1 g. (cf. *C. A.* 6, 2428). To 10 g. unfractionated **B**, previously purified with $EtOAc$ and dried *in vacuo* over P_2O_5 at 100° , were added 40 cc. $AcOH-HBr$ soln.; the flask was protected with $CaCl_2$ and was kept at room temp. for 8 days; the contents were stirred once each day; 10 cc. $AcOH$ were added and the 3.5 g. of **H** which sepd. were removed; $AcBr$ was added slowly to the filtrate until portions poured upon ice and dissolved in Me_2CO gave no color with $FeCl_3$; the reaction mixt. was poured upon ice, filtered and the pptd. **C** washed with ice water, pressed on a porous plate and dried *in vacuo*; purified by pouring a $CHCl_3$ soln. into cold Et_2O , it forms an amorphous white material which is readily sol. in Me_2CO , $EtOAc$ or $CHCl_3$, very slightly sol. in $MeOH$ or $EtOH$ and insol. in Et_2O . **E** is obtained when **C** is heated 0.5 hr. to 100° with 10 parts Ac_2O and 1 part $AcONa$, poured on ice, washed with H_2O , dried *in vacuo*, dissolved in $CHCl_3$, added to $EtOH$ at -15° , filtered and washed with $EtOH$ and Et_2O ; it is sol. in Me_2CO , $CHCl_3$ or $EtOAc$, slightly sol. in hot abs. alc., insol. in H_2O , softens 110° and m. $130-5^\circ$, $[\alpha]_D^{25}$ 32.67° (Me_2CO). **C** in abs. $MeOH$ was boiled 0.5 hr. with Ag_2CO_3 , filtered hot, evapd. to dryness *in vacuo* and reacylated in C_2H_5N with Ac_2O ; after 24 hrs. the mixt. was poured into H_2O , the ppt. washed with dil. $AcOH$ and then H_2O , and dried, and **F** pptd. by adding a $CHCl_3$ soln. to cold $EtOH$ and recrystd. from $EtOH$. **D** when treated with $AcOH-HBr$ and then with $AcBr$ similarly yields **C**, ($[\alpha]_D^{16}$ 58.83° (Me_2CO)), which on treatment with Ac_2O and $AcONa$ gave a 98% yield of **E**, $[\alpha]_D^{25}$ 44.67° (Me_2CO); this sample of **E** from **D** similarly yields **F**, $[\alpha]_D^{15}$ 31.52° (Me_2CO). **E** in $MeOH$ on hydrolysis with HCl gave an impure tetragalloyl glucose, $[\alpha]$ 49.8° ($FtOH$). In a similar manner the following were obtained from 10-g. fractions of **B**: 7.86 g. **E**, $[\alpha]_D^{18}$ 27.37° (Me_2CO) from the fraction $[\alpha]$ 30° ; 8.74 g. **E**, $[\alpha]_D^{15}$ 43.78° , from the 80° fraction; 8.9 g. **E**, $[\alpha]_D^{18}$ 44.18° , from the $130-5^\circ$ fraction; **C** from the 130.5° fraction gave $[\alpha]_D^{16}$ 59.5° and **E** from this fraction gave $[\alpha]_D^{16}$ 31.81° ; a 10-g. sample of **B**, fraction $[\alpha]$ $145-7^\circ$, gave 8.83 g.

E, $[\alpha]_D^{18}$ 44.30°. A triacetylalloyl- α -methylglucoside was prepd. by condensing 5 g. α -methylglucoside, dried *in vacuo* over P_2O_5 , 36.4 g. triacetylalloyl chloride, 18.2 g. quinoline, freshly distd. from BaO, and 75 g. $CHCl_3$ distd. over P_2O_5 ; after 48 hrs. the mixt. was washed with 2 portions of dil. H_2SO_4 , then 3 portions of H_2O , dried, evapd. *in vacuo* and poured into 500 cc. EtOH; crystd. from EtOH, it gave $[\alpha]_D^{18}$ 42.36° (Me₂CO). Triacetylalloyl- β -methylglucoside, similarly prepd. from β -methylglucoside, is sol. in Me₂CO, $CHCl_3$, slightly sol. in EtOH, softens 110°, m. 150–60° and gave $[\alpha]_D^{18}$ 32.9° (Me₂CO).

N. A. LANGE

Reaction of alcohols with bromomethylphthalimide and its use for the separation and identification of alcohols. H. H. HOPKINS. *J. Am. Chem. Soc.* **45**, 541–4 (1923); cf. Pucher and Johnson, *C. A.* **16**, 1573.— $C_6H_4(CO)NCH_2Br$ gives well crystd. derivs. with a no. of alcs. but is not entirely satisfactory for their identification because the alcs. must be perfectly dry for satisfactory results and they must be present in excess; furthermore, moisture immediately decomp. the A into $C_6H_4(CO)_2NCH_2OH$ before it can react with the alcs. The following phthalimidomethyl alkyl ethers, $C_6H_4(CO)_2NCH_2OR$, were prepd.: methyl, m. 118°; ethyl, m. 86°; propyl, m. 52–3°; isopropyl, m. 92–3°; lactic acid, m. 185°; phenyl, m. 171–2°, glyceryl, $C_3H_5O_3[CH_2N(CO)_2C_6H_4]_3$, m. 174–5°. MeOH can be sep'd. from Me₂CO by means of the compd. it forms with A. Of the Me, Et and Pr compds., resp., 0.25 g. dissolves in the following no. of cc. of various solvents: EtOH 40, 20, 10; MeOH 10, 2, 1; C_6H_6 3, 1, 1; Et₂O 40, 2, 1; Me₂CO 2, 1, 1.

C. A. R.

Union of hydrogen with acetylene derivatives. XIV. Hydrogenation of phenylacetylene. I. S. ZALKIND. *J. Russ. Phys. Chem. Soc.* **52**, 191–8 (1920); cf. *C. A.* **11**, 584.—The velocity of hydrogenation of $PhC\equiv CH$ in the presence of colloidal Pt increases to a max. after combination of the first 2 atoms of H and subsequently diminishes. The reaction proceeds, but extremely slowly, after 4 atoms of H have been combined; characteristic of this late stage of the hydrogenation is the fact that it proceeds more rapidly with low than with high concns. of the catalyst. Further, hydrogenation of the triple to the double linking takes place more slowly than that of the double to the single linking. The results of expts. with styrene indicate that, in the nascent state, this compd. is more readily hydrogenated than when ready-formed. Here too, the hydrogenation does not cease when the side-chain is converted into the Et group, but is continued at the expense of the double linkings of the nucleus. It seems possible, indeed, that the initial stage of the reaction proceeds in two different directions, yielding, not merely $PhEt$, but also 5-methyl- $\Delta^{1,3}$ -cyclohexadiene.

J. C. S.

Some derivatives of isoeugenol. G. RASVELLI. *Gazz. chim. ital.* **52**, **II**, 129–30 (1922).—In connection with other work the following 4 new derivs. of isoeugenol were prepd. 5 g. acetylisoegenol (A) were treated in $CHCl_3$ with a slight excess of Br₂ in $CHCl_3$. On evapn. the soln. dibromoacetylisoegenol was obtained as crystals from ligroin, m. 125° and blackens in the light. Dibromoacetylisoegenol was similarly obtained as scales, m. 113°, stable in light. 2 g. A in Et₂O were treated with 2.6 g. I₂ in Et₂O and some $HgCl_2$ as catalyst. After 24 hrs. the soln. was washed with H_2O , then with SO_2 soln. to eliminate I₂ and finally with H_2O . On evapn. there sep'd. an iodoacetylisoegenol (probably the diiodo deriv.), decompd. easily. Diiodobenzoyleisoeugenol was obtained similarly as needles, m. 85–6°.

E. J. WITZEMANN

Preparation of cyclic amines. ALPHONSE MAILHE. *Bull. soc. chim.* **33**, 83–6 (1923); cf. *C. A.* **16**, 1942.—The synthesis of amines by hydrogenation of hydrazones and ketazines has been extended to the prepn. of cyclic primary amines; the reaction is general, and the products are always accompanied by small amts. of the corresponding sec. amines. 1,3-Dimethyl-4-cyclohexanone (A), b. 176.5°, prepd. by hydrogenation of 1,3,4-xylenol and oxidation of the resulting 1,3-dimethyl-4-cyclohexanol was converted

to its *hydrazone* (B) by boiling 6 hrs. with $(\text{NH}_2)_2\text{H}_2\text{O}$ and a little EtOH, distg. the alc., and adding H_2O and Na_2CO_3 ; B is an oil, b. 225° , which, when conducted in vapor form with a strong current of H over reduced Ni at 180° , gives mainly 1,3-dimethyl-4-cyclohexylamine (C), b. $169-71^\circ$, $d_{15} 0.8810$, forming a carbonate on exposure to air, and in Et_2O a hydrochloride, needles m. 278° (darkening); it gives a carbylamine reaction, reduces cold AgNO_3 , ppts. $\text{Cu}(\text{OH})_2$ from CuSO_4 and gives a substituted phenylurea, m. 174° , with PhNCO in ligroin; a small amt. of bis[dimethylcyclohexyl]amine, alk. to litmus, forming a HCl salt, is also formed along with C. When carvone ketazine, a viscous oil from 2 mols. carvone and 1 mol. $(\text{NH}_2)_2\text{H}_2\text{O}$, is led in vapor form with H over reduced Ni at $190-200^\circ$ it gives carvylamine (D) and a small amt. of dicarvylamine. D b. $205-10^\circ$, $d_{15} 0.8813$, strongly alk. to litmus, carbonating readily in air; the hydrochloride, from Et_2O by evapn., forms beautiful brilliant leaflets, m. 198° . Menthone reacts with $(\text{NH}_2)_2\text{H}_2\text{O}$, giving the hydrazone (E), with a little ketazine. When E, b. 243° , is led with H over Ni at 200° it is easily reduced to menthylamine (F) and a little dimethylamine (G). F is a strong base, b. 212° , carbonating rapidly in air, reducing cold AgNO_3 , pptg. $\text{Cu}(\text{OH})_2$ from CuSO_4 ; the hydrochloride m. 274° . G, b. $305-10^\circ$, is strongly basic, does not ppt. $\text{Cu}(\text{OH})_2$, and reduces cold AgNO_3 only slowly; the crystalline hydrochloride m. 207° .

A. R. ALBRIGHT

The oxidation of α, α -allylmethylcyclohexanone by permanganate. R. CORNBURY.

Bull. soc. chim. 31, 698-712(1922).—The ketone, $\text{CH}_2(\text{CH}_2)_2\text{CO.CMeCH}_2\text{CH}_2\text{CH}_3$, oxidized with aq. alk. KMnO_4 , gives a mixt. of products which may be sepd. by distn. into neutral and acid fractions. The neutral fraction probably contains the ethylenic oxide deriv. of the ketone. Oxidation by KMnO_4 in the presence of soda lime gives the corresponding glycol, its ether, and undetermined acid, and a polymer of the ethylenic oxide compd. It was not possible to investigate the products exhaustively.

JAMES A. BRANLEY

Napthenic acids derived from Japanese petroleum. YOSHIO TANAKA AND SHOICHIRO NAGAI. J. Am. Chem. Soc. 45, 754-6(1923).—From the waste lye obtained in the refining of a 25-6° B ϕ . "neutral distillate" of an Akita-Kurokawa crude oil were isolated trideca-, tetradeca- and pentadecanaphthenic acids, with the following consts., resp.: $b_{4.5-5.5} 167-9^\circ$, $178-80^\circ$, $191-2^\circ$, $d_{15}^{25} 0.9016$, 0.9930 , 0.9941 , $n_D^{15} 1.4784$, 1.4807 , 1.4848 . They were sepd. by fractionation of their methyl esters whose resp. consts. are: $b_{4.5-5.5} 124-6^\circ$, $135-7^\circ$, $147-9^\circ$, b. $262-3^\circ$, $277-8^\circ$, $296-7^\circ$, $d_{15}^{25} 0.9622$, 0.9644 , 0.9659 , $n_D^{15} 1.4663$, 1.4686 , 1.4728 .

C. A. R.

Presence of the glucoside of an essential oil in the foliated stems and roots of *Sedum telephium* L. M. BRIDEL. J. pharm. chim. 26, 289-98(1922).—Applying to the foliated stems and roots of *Sedum telephium* L. Bourquelot's biochem. method, B. obtains a glucoside (A) yielding upon hydrolysis with emulsin an essential oil of rose odor; hydrolysis with H_2SO_4 gave an odor of eucalyptol or terpineol. This suggests a substance close to geraniol, which easily isomerizes with acids into terpene products. An amorphous form of A is sol. in H_2O , EtOH, EtOAc, acetone and CHCl_3 . In H_2O it slightly reduces Fehling soln. (1 g. is equiv. to 0.103 g. dextrose); $[\alpha]_D -28.57^\circ$. The reducing sugar formed simultaneously with the essential oil was identified as dextrose by soln. in MeOH and conversion into crystd. β -Me glucoside under the influence of emulsin.

S. WALDBOTT

Effect of fuller's earth on pinene and other terpenes. CHAS. S. VENABLE. J. Am. Chem. Soc. 45, 728-34(1923).— α -Pinene in the presence of fuller's earth first undergoes a mol. rearrangement; among the products formed are dipentene and terpinene; no camphene was found. The second stage of the reaction is a polymerization to dipinene and various polyterpenes. At high temps. the dipinene so formed slowly

decomps. into low boiling paraffin hydrocarbons and some *p*-cymene. The reaction is general for terpenes and unsatd. oxygenated terpenes. Oxygenated diluents (Me_2CO , alc., Et_2O and especially H_2O) exert a strong inhibiting influence on the reaction, while such diluents as C_6H_6 and CCl_4 apparently retard the reaction only in so far as they reduce the concn. of the pinene. Iron and silica gels and activated charcoal do not promote the reaction.

C. A. R.

Sulfur-terpene substitution compounds. W. B. PRATT. *J. Ind. Eng. Chem.* 15, 178-81 (1923).—S acts upon terpenes, such as the α -pinene of turpentine, to form viscous or brittle masses, contg. 40-50% of S. The action is accompanied by the evolution of H_2S , and hence is probably one of substitution. The products are of value in treating cotton goods with which rubber is later to be calendered.

T. S. CARSWELL

***tert*-Phenylcamphenilol**, its transformation into phenyl- α -*peri*-cyclopocamphane and then into phenylapocamphor. MARIA BREDTSAVELSBERG. *Ber.* 56B, 554-61 (1923).—This work is a part of a general study of the splitting off of H_2O from *tert*. alcs. of the camphane, fenchane and camphenilane series. In order to introduce a substituent which would not furnish a H for the splitting off of H_2O , Ph was introduced by means of PhMgBr , giving *tert*-phenylcamphenilol, b_4 122°, b_{13} 160-6°, $d_4^{15.4}$ 1.0717; n_D^{20} 1.55518. The prepn. from optically active camphenilone showed $[\alpha]_D^{20}$ 11.2°. The alc. b. about 276° (slight decompn.) and reacts only slowly with Na. PCl_5 or SOCl_2 gave a mixt. of chloride and hydrocarbon which could not be sepd. Phenyl- α -*peri*-cyclopocamphane is best obtained by heating the alc. with Ac_2O in a sealed tube for 25 hrs. at 170-80°; it b_4 96-7°, $d_4^{19.25}$ 1.00609, $n_D^{19.25}$ 1.54710. The compd. from the active alc. is nearly inactive. It is very stable towards KMnO_4 . Treated with 8 parts AcOH and a few drops of H_2SO_4 for 48 hrs. at 60-65°, it gives phenylapoisborneol acetate, b_4 142-3°, d_4^{20} 1.06888; n_D^{20} 1.53003. If the hydrocarbon is heated with HCO_2H for 50 hrs. at 75° in a sealed tube, the *formate* results, b_4 127-8°. Sapon. by heating under pressure gave the alcohol, $\text{C}_{16}\text{H}_{24}\text{O}$, b_4 145°, $d_4^{21.2}$ 1.0666; $n_D^{21.2}$ 1.55518. Oxidation with CrO_3 - H_2SO_4 is very difficult, and the phenylapocamphor, b_4 143°, must be sepd. as the *semicarbazone*, decomps. 199°. The oxidation to phenylapocamphoric acid, m. 206°, is more readily carried out than that to the ketone, using alk. KMnO_4 at 80°. Distn. gives the anhydride, m. 208-9°.

C. J. WESR

Camphor series II. SHIGERU KOMATSU. *Mem. Coll. Sci. Kyoto Imp. Univ.* 6, 55-7 (1922).—The work was undertaken to give evidence in support of the assumption that the formation of *l*-isocamphane from *d*- and from *l*-camphor is attended by the intermediate formation of camphene. The sapon. of the Et, menthyl and bornyl esters of bornylacetic acid, obtained from *d*-camphor by the Reformatsky synthesis, gives the same *l*-isobornylacetic acid. The reduction of *d*-camphor oxime gives *d*-bornyl- and *l*-isobornylamines in the ratio of 66 to 34. With NH_3 at 400° *d*-borneol gives a product consisting mostly of *d*-camphene. In the same manner *l*-borneol is transformed into *l*-camphene. To prove the camphene was derived from bornylamine formed temporarily by the interaction of borneol and NH_3 and not directly from borneol by the Wagner rearrangement it was shown that *d*-bornylamine on heated thoria decompd. into *d*-camphene and NH_3 . *l*-Isocamphane is formed from both *d*- and *l*-camphene by catalytic hydrogenation. The following scheme represents the changes which take place in the catalytic hydrogenation of *d*- and *l*-camphor:

| | | |
|--------------------|-----------|--|
| <i>d</i> -camphor | reduction | $\left\{ \begin{array}{l} d\text{-borneol} \\ l\text{-isoborneol} \end{array} \right.$ |
| <i>d</i> -camphene | reduction | $\left\{ \begin{array}{l} d\text{-isoborneol} \\ l\text{-borneol} \end{array} \right.$ |
| <i>l</i> -camphene | reduction | <i>l</i> -isocamphane |

(1) Synthesis of *l*-isobornylacetic acid and its esters. KIYARO FUJŌ. *Ibid* 57-62.—*Et*-isobornylacetate, b_4 108-12°, $[\alpha]_D^{20}$ -24.97°, was obtained in 20.2% yield by the Reformatsky synthesis from 11 g.

Mg, 32 g. *d*-camphor in alc. and $\text{CH}_3\text{CO}_2\text{Et}$. The organo-Mg compd. thus formed was decompd. with ice-cooled dil. H_2SO_4 , extd. with Et_2O , the Et_2O distd. off and the residue steam-distd., extd. with Et_2O and distd. under reduced pressure. In a similar way *l*-menthyl *l*-isobornylacetate and *d*-bornyl *l*-isobornylacetate, m. 196–7°, were prepd. The free acid, sol. in H_2O and alc., decompd. with heated H_2SO_4 to an unsatd. compd., was obtained from its esters by hydrolysis with satd. $\text{Ba}(\text{OH})_2$ in EtOH , and decompn. of the Ba salt with 10% H_2SO_4 . The Ba salt, $[\alpha]_D^{25}$ 9.53–12.91°, and the NH_4 salt are sol. in H_2O and the Ag salt is insol. (2) Bornylamine and its transformation into isocamphene. SHOZO YAMAGUCHI. *Ibid* 62-5.—The reduction of *d*-camphor oxime with Na in abs. iso-AmOH, acidification with HCl, evapn. of the alc. and crystn. gave a mixt. of the HCl salts of *d*-bornyl- and *l*-isobornylamine. The *d*-compd., $[\alpha]_D^{25}$ 24.7°, was sep'd. from the mixt. by conversion into the sulfonates with Ag *d*-camphorsulfonate, fractional crystn., hydrolysis with KOH and treatment with HCl. The % of the 2 compds. in the hydrochloride mixt. (65.9 of *d*- and 34.1 of *l*-) was found from the rotatory power. *d*-Camphene was extd. with Et_2O from a product obtained by passing bornylamine (96.2% of *d*- and 3.8% *l*-compd.) on thoria heated to 400°. (3) Catalytic preparation of camphene and isocamphene. RISABURO NAKAI. *Ibid* 65-72.—The dark-yellow liquid obtained by passing *d*-borneol and NiH_2 over thoria heated to 400° was treated with HCl, steam-distd., made alk. with NaOH, and distd. with steam to remove basic substances, the Et_2O ext. from which gave the carbylamine reaction. The first distillate, the main part of the product, was distd. and the fraction b. 130–350° sep'd. into 8 fractions by further distn. Each of these fractions was analyzed and the d., $[\alpha]$ and *n* det'd. The 1st fraction, 135–50°, consisted of an aromatic hydrocarbon, the last, 180–205°, of a mixt. of borneol and the hydrocarbon $\text{C}_{10}\text{H}_{18}$ and the 3rd, 158–62°, of pure *d*-camphene. *l*-Camphene was obtained from *l*-borneol in a similar way. The same *l*-isocamphene was obtained by the reduction of either *d*- or *l*-camphene with H_2 in the presence of Ni.

G. W. STRATTON

Structure of benzidine. ROGER ADAMS, J. E. BULLOCK AND W. C. WILSON. *J. Am. Chem. Soc.* 45, 521-7 (1923).—*m*- and *p*- $\text{C}_6\text{H}_4(\text{CHO})_2$ and resoracetophenone combine in boiling alc. with benzidine (A) to form compounds having a compn. corresponding to 1 mol. each of the 2 components minus 2 mols. H_2O . Dianisidine forms a similar compound with A, and terephthalaldehyde monazine, m. 232°, from the aldehyde and 0.5 mol. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in alc., gives with A a compound of the compn. $(\text{N}:\text{CHC}_6\text{H}_4\text{CH}:\text{NC}_6\text{H}_4)_2$. None of these compds. is sol. to any extent in the ordinary org. solvents and none melts or decomp. below 275°; owing to their slight soly., their mol. wts. could not be det'd. It seems probable that the C_6H_4 rings in Ph_2 derivs. are in motion, with the limiting positions represented by the 2 possible Kautler formulas and the intermediate position by the formula usually assigned to Ph_2 . Terephthalaldehyde dihydrazone, from the aldehyde and 3 mols. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in alc., m. 165° (decompn.) with formation of a substance which does not m. below 300°.

C. A. R.

Condensation of benzidine with formaldehyde. H. KONDO AND S. ISHIDA. *J. Pharm. Soc. Japan*, No. 489, 979-85 (1922).—In order to study the nature of the intermediate product of condensation of benzidine with CH_2O , K. and I. treated 10 g. benzidine in 200 cc. abs. alc. with 30 cc. of 35% CH_2O (cf. Schiff, *Ber.* 25, 1936 (1892)), and obtained a white granular ppt. which, when heated at 60–70° for 30 min., washed with alc. and dried, m. 271–2°. It is non-cryst., insol. in alc. and H_2O , contains 2 mols. of CH_2O in the form of hydroxymethylene imide, and is dihydroxymethylenebenzidine (A). S. obtained under similar condition dimethylenebenzidine, crystals, m. 140–1°. When A is dissolved in dil. HCl, a trace of a red brownish non-cryst. substance, giving a CH_2O odor is produced. On addn. of concd. HCl to this dil. HCl filtrate, there are obtained needles of monohydroxymethylenebenzidine (B) whose m. p. was so high that

it could not be detd. During the condensation of benzidine with CH_3O , therefore, 5 products are possible: $\text{H}_2\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{NHCH}_2\text{OH}$ (B); $\text{H}_2\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{N}:\text{CH}_2$; $\text{HOCH}_2\text{NHC}_6\text{H}_4\text{C}_6\text{H}_4\text{NHCH}_2\text{OH}$ (A); $\text{CH}_2:\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{NHCH}_2\text{OH}$, and $\text{CH}_2:\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{N}:-\text{CH}_2$ (Schiff). S. T.

Formation of triphenylparosaniline hydrochloride from diphenylamine and chloralammonia. RIKI HORITUCHI. *Mem. Coll. Sci. Kyoto* 5, 1-7 (1921).—The small yield of triphenylparosaniline-HCl obtained by heating Ph_2NH and chloralammonia directly at 130° is greatly increased by maintaining the temp. at 100° for some time prior to heating at 130° . H. has investigated the reaction of PhNH_2 with various compds. contg. CCl_3 and CHO groups, resp., and concludes that compds. contg. the former group are alone concerned in the formation of diphenylamine-blue, the Cl atoms being replaced by the Ph group, and the resulting product reacting with part of the HCl produced. J. C. S.

Phenolsulfonephthalein and some of its derivatives. W. R. ORNDORFF AND F. W. SHERWOOD. *J. Am. Chem. Soc.* 45, 486-500 (1923).—Pure cryst. phenolsulfonephthalein (A) (mostly prepd. by heating the chlorides of *o*- $\text{HO}_2\text{SC}_6\text{H}_4\text{CO}_2\text{H}$ with an excess of PhOH without a condensing agent) was obtained by repptg. from cold NaHCO_3 ; some was also recrystd. from AcOH . The pure anhyd. A is probably an inner oxonium or carbonium salt and the cryst. air-dried product, which always contains about 1.26% H_2O , seems to be a solid soln. of this inner salt and the quinonoid hydrate. The NaHCO_3 -insol. but NaOH -sol. product always formed along with A contains only 0.5 as much S as A and seems to be formed by the action of PhOH on A. The filtrate from the crude A also contains *p*-hydroxybenzylbenzene-*o*-sulfonic acid (prepd. for comparison from $\text{HO}_2\text{CC}_6\text{H}_4\text{SO}_3\text{NH}_4$ heated with PhOH), pink leaflets with 1 H_2O , drying even at 80° to the red quinonoid anhydride $\text{O}:\text{C}_6\text{H}_4:\text{C}(\text{C}_6\text{H}_4\text{SO}_2\text{O})$ and decomp. at $135-40^\circ$ into H_2O ,

A and sulfobenzoic anhydride; it also forms A when heated with PhOH and is probably an intermediate product in the formation of A. Like other phthaleins, A yields colorless lactoid and colored quinonoid derivs. There were prepd. the colored *mono*- and *diammonium* and *-sodium* salts, and the colorless *diacetate*, m. 165° , and *dibenzoate*, m. $185-6^\circ$ (decompn.). With PhNH_2 at $140-50^\circ$ A gives the green *diphenylaminesulfonephthalein* (B), $\text{PhNHHC}_6\text{H}_4\text{C}(\text{C}_6\text{H}_4:\text{NPh})\text{C}_6\text{H}_4\text{SO}_3\text{H}$, a reaction so characteristic that it may be used as a test for A. Reduction of A with Zn dust in boiling H_2O gives the amorphous colorless *phthalin* (*dihydroxytriphenylmethanesulfonic acid*). The colorless *monomethyl ether* of A, m. 178° , obtained from A in boiling alc. HCl, and the *ethyl ether*, m. 171° , change into the colored quinonoid ethers when heated at 170° ; the colorless forms do not combine with NH_3 while the colored ethers form stable *monoammonium salts*, showing that they contain a free SO_3H group. Pure tetrahromophenolsulfonephthalein (C), crystd. from C_6H_6 and glacial AcOH , m. 279° and is colorless, and therefore has the lactoid structure; it forms no compd. analogous to B with PhNH_2 ; it yields a red *hydrate* with $4\text{H}_2\text{O}$ which dries *in vacuo* to the light brown quinonoid form of C and is reconverted into the lactoid form on heating; it gives colored *diammonium* and *mono*- and *disodium salts* and a colorless *diacetate*, m. 234° , and *dibenzoate*, decomp. 270° ; with NaOMe and MeI and MeOH it yields a colored *monomethyl ether*, m. 293° , which does not react with boiling PhNH_2 but forms an unstable yellow *hydrochloride* and a blue *monoammonium salt*. C. A. R.

Bromination products of asym-diphenylethylene. P. LIPP. *Ber.* 56B, 567-71 (1923).—In order to gain further light upon the behavior of camphene upon bromination, simpler compds. have been studied. $\text{Ph}_2\text{C}:\text{CH}_2$, b_p 139° , readily adds Br in CS_2 with little or no evolution of HBr , forming *1,1-diphenyl-1,2-dibromoethane*, compact plates from petrol. ether, decomp. $63-4^\circ$ (corr.), with the formation of $\text{Ph}_2\text{C}:\text{CHBr}$; with MeOH -

KOH the Br in the 1-position is replaced by MeO, giving the *1-methoxy derivative*, compact, short prisms and plates, m. 73–4.5°; *ethoxy derivative*, long prisms, m. 98–9°. $\text{Ph}_2\text{C}:\text{CHBr}$ fused with KOH, gives a very good yield of $(\text{PbC})_2$. CO_2 with the Grignard reagent from $\text{Ph}_2\text{C}:\text{CHBr}$ gives, as the main product, $\text{Ph}_2\text{C}:\text{CHCO}_2\text{H}$ and, in much smaller yield, $(\text{Ph}_2\text{C}:\text{CH})_2$. C. J. WHEAT

Dinitrobenzil. E. DE BARRY BARNETT AND L. J. KAY. *Chem. News* 125, 57–8 (1922).—Dinitrobenzil may be obtained in almost theoretical yield and very pure by nitration of benzil with a mixt. of H_2SO_4 and HNO_3 . Details of the prepn. are given. Although dinitrobenzil has two CO groups, it forms only a *monophenylhydrazone*, m. 159° (decompn.), under ordinary conditions. Attempts to prep. a tetranitro deriv. from dinitrobenzil by further nitration were unsuccessful. J. C. S.

Thermochemical researches on oximes. I. Ketoximes not exhibiting stereoisomerism. ALICJA DORABIALSKA. *Roczniki Chemji* 1, 424–47 (1921).—The heats of certain reactions of some ketoximes are measured. From the results so obtained, and from those obtained previously (W. Swientoslawski, *C. A.* 12, 1640), various generalizations are made. The ketoximes used were acetoxime, $\text{PhMeC}:\text{NOH}$, and $\text{Ph}_2\text{C}:\text{NOH}$. The chief reactions studied are the formation of the HCl salt of the oxime, its soln. in 10% NaOH, and the formation of the Na salt of the oxime. The results obtained, together with those calcd. from these, are given in the following table, where q_{HCl} is the heat of formation of the HCl salt in Et_2O and q'_{HCl} that in H_2O . The heat of the soln. of the HCl salt in 10% NaOH is Q_{HCl} , in water, S_{HCl} . The heat of soln. of the oxime in dil. NaOH soln. is q , in water S , in ether S' . The degree of hydrolysis of Na salts of these oximes is given as $\nu\%$. Results are expressed in cal. per millimole. In the

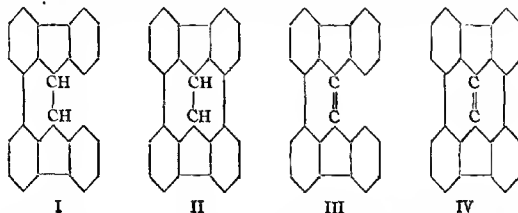
| | q_{HCl} | q'_{HCl} | q | $\nu\%$ | Q_{HCl} | S | S_{HCl} | S' |
|----------------------------------|------------------|-------------------|------|---------|------------------|-------|------------------|-------|
| Acetoxime | 10.93 | 1.19 | 5.70 | 39.6 | 17.16 | –1.28 | –1.95 | –2.89 |
| $\text{PhMeC}:\text{NOH}$ | 8.17 | 0.51 | 6.34 | 40.3 | 16.52 | –2.98 | –3.52 | — |
| $\text{Ph}_2\text{C}:\text{NOH}$ | 7.71 | — | 5.80 | — | 12.51 | –4.06 | –6.99 | — |

case of $\text{PhMeC}:\text{NOH}$, the HCl salt prepd. at diff. temps., and from different media, gave the same Q_{HCl} , thus showing that no stereoisomeric modification of this oxime is produced under the conditions in question. Conclusion: The heat of formation of the HCl salts of the ketoximes differs little from that of the aldioximes, and diminishes as the acidity of the ketoxime increases. The heat of soln. of these HCl salts diminishes with increasing acidity of the ketoxime, owing to a parallel increase in the negative heat of the soln., and decompn. of the former in water. Finally, the negative heat of soln. of ketoximes in water appears to be greater than that of aldioximes. II. The stereoisomeric ethyl esters of oximinooacetoacetic acid. *Ibid* 448–67.—Etl oximinooacetoacetate has been described by Jovitschitsch who states that it may exist in 2 forms, hotb oils. The β -form, according to him, differs from the α -, in that its NaOH soln. on acidification evolves CO_2 . The conversion is stated by him to be effected by the action of HNO_3 and H_2SO_4 on the ester. Bouveault and Wahl (*Bull. soc. chim.* 33, 559–61 (1905)), however, obtained only one form, m. 56°, and D. finds that no conversion is effected by their method. The α -isomeride is prepd. in various ways, including a hitherto undescribed method, whereby it is obtained from NOCl and $\text{AcCH}_2\text{CO}_2\text{Et}$. The purest form m. 56.7°. A *monohydrate*, m. 45°, is obtained in rhombic plates, and from analyses of the compd. m. 56.7° it is concluded that it contains at least 28.7% of the hydrate, which can be isomorphous with it, and has the same space structure. It is found that if the α -isomeride be left in strongly acid soln., and this is extd. with ether, a new modification is obtained, m. 49°. This is the β -ester, mixed with, at the very least, 19% of the α -form. On soln. in alkalis and reprecipn., the α -form is regenerated. Attempts to produce a HCl salt failed. Both forms were examd. thermochem. The reactions studied were

the formation of the Na salt of both forms, from solns. and from the solid esters. Further, the heat of reaction with HCl in ether, g_{HCl} , was measured, and that of the soln. of oximes in water (S). The following values were obtained for the α -ester: g 8.85, g_{HCl} 2.86, Q 4.83, and S -3.77, and for the mixed α,β -ester: g_{HCl} 4.96, Q 6.14, and S -3.70. The heat of formation of the Na salt is, for solns. of the esters, given by g , and with solid esters by Q , all figures being given in cal. per millimole. For the β -esters, g is calcd. to be 6.72, while for the monohydrate it is 8.77. The degree of hydrolysis of the Na salt is found to be zero. The heat of reaction of the ester with NOCl is 31.77 cal. per millimole. J. C. S.

Experiments on azulene. R. E. KREMER. *J. Am. Chem. Soc.* 45, 717-23 (1923).—The azulene, isolated from oil of milfoil by a slight modification of Sherndal's method, $b_{11.5}$ 185.6°, $b_{11.5}$ 167-8.4°, d_{25}^{25} 0.98771, d_{25}^{25} 0.98465; the absorption spectrum (limits of transmission for various thicknesses of soln.—the solvent is not stated) is given. Reduction with Pd-H shows that it is bicyclic, giving a colorless compound, $C_{15}H_{12}$, b_{25} 130-40°, d_{25} 0.8920, n_D 1.4870, r 0.3224 (Lorenz and Lorentz formula). Alk. $KMnO_4$ gives CO_2 , Me_2CO , $AcOH$ and a homolog of phthalic acid. It behaves like an unsatd. compd. towards Br , N_2O_5 and $NOCl$ but no well defined products were obtained. The heptane soln., on standing over Na, becomes decolorized and deposits a brown crust on the metal; addn. of alc. and H_2O regenerates the azulene. A benzofulvene structure, $MeC_6H_4.CMe:CMe:CMe_2$ or $MeC_6H_4.CHMe.C(-CH_3).C:CMe_2$, is tentatively assigned to azulene. C. A. R.

The pyrogenic transformation of fluorene. K. DZIEWONSKI AND J. SUSZKO. *Roczniki Chemii* 1, 387-410 (1921).—Fluorene vapor is passed under reduced pressure, through a quartz tube heated to redness and contg. a coil of wire. The vapors condense to an oily solid, mainly unchanged fluorene, but contg. 3 other hydrocarbons, of the empirical formulas $C_{22}H_{16}$, $C_{24}H_{18}$, and $C_{26}H_{20}$. Graebe (*Ber.* 25, 3146-9) obtained a substance, $C_{26}H_{20}$, by passing fluorene vapors over heated PbO , but this substance, bidiphenylene-ethylene, is shown to be different from the substance of the same empirical formula obtained by the authors. This hydrocarbon, *difluorenylene* (I), forms prisms, m , 218°, and is identical with the hydrocarbon, $C_{26}H_{20}$, obtained by Klings and Lomnes [*Ber.* 29, 2152-56 (1896)] from tetraphenylenepinacolin, to which an asym. structure was wrongly assigned. The *picrate*, reddish brown needles, m , 202-3°, the *dinitro deriv.*, m , 360-5° (decompn.), and *dihydroxy deriv.*, colorless, rhombic plates, m , 269°, were prepd. The 2nd hydrocarbon, *dihydorubicene*, $C_{24}H_{18}$ (II), needles, m , 296°, is obtained in small quantity only. The *picrate*, orange needles, m , 354-6°, is unstable.



The 3rd product, rubicene, $C_{26}H_{20}$, deep red needles, m , 305°, seems to be best prepd. by this method. Pummerer (*C. A.* 6, 1006), who prepd. it from phenanthraquinone, assigned to it the empirical formula $C_{26}H_{20}$ and the structure III; this is shown to be incorrect, and the structure IV is assigned to it. The *picrate*, reddish brown needles, m , 258°, is unstable; the *dinitro deriv.*, brick-red needles, m , 440-2° (decompn.), and the

di-bromo deriv., brownish red needles, m. 378° (decompu.), were prepd., also a *rubicene-disulfonic acid*, which is found to act as an acid dye. Attempts to reduce the hydrocarbon did not lead to any definite results, while oxidation with CrO_3 mixt. gives a yield of only 5% yellow plates, m. 203°, and of a feebly acid nature. J. C. S.

Correction of our work: "Investigations and ring closures in the series of the methylnaphthalenes." FRITZ MAVER AND ADOLF SIEGLITZ. *Ber.* 55B, 2940(1922); cf. *C. A.* 17, 99.—The $1,4\text{-C}_{10}\text{H}_6(\text{CO}_2\text{H})_2$ had already been prepd. by Scholl and Neumann (*C. A.* 16, 2142); when it is recrystd. from PhNO_2 its m. p. is raised to the temp. (309°) given by them. $1,4\text{-C}_{10}\text{H}_6\text{McBz}$ m. 74-5°, not 174-5°. The 4-methyl-*periben-zanthrone* obtained from the ketone m. 193-4°, not 115°. $1,2\text{-C}_{10}\text{H}_6\text{BzMe}$ b₁₅ 140-5°, not 240-5°. In formula II on p. 1837 of the original paper (formula III in the abstr.) the CO and CH₂ groups should be transposed and the name of the compd. it represents changed to 2-ethyl-4,5-benzo-3-indanone. C. A. R.

Spectrochemical investigation of the polynuclear aromatic compounds in solution. F. KROLLFEIFFER. *Ann.* 430, 161-229(1923).—The historical introduction gives approx. 100 references to earlier work and discussion. In general spectrochem. investigation can be carried out only on compds. which m. below 100°. In other cases a solvent must be used. Of 13 solvents for C_{10}H_8 which were investigated, BzOAm , *m*- $\text{Me}_2\text{C}_6\text{H}_3\text{OH}$, BzMe , $\text{C}_6\text{H}_7\text{N}$, PhNEt_3 , PhNH_2 and *o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{Me})_2$ were suitable, but when tested on $1,4\text{-C}_{10}\text{H}_6\text{Cl}_2$, $\text{C}_6\text{H}_7\text{N}$ alone proved satisfactory, and was adopted for the remainder of the work. Tables are given which contain the numerical results of the investigation of C_{10}H_8 and derivs. (23), C_8H_6 derivs. (18), compds. with 2 C_6H_5 nuclei, alone and in $\text{C}_6\text{H}_7\text{N}$ (8), $\text{C}_{14}\text{H}_{10}$ and derivs. (5), d , n for α , β and γ , M , etc. being given. The original must be consulted for this mass of detail. The spectrochem. value of the dissolved substance is independent of the concn. of the soln. General rules for the selection of the optically suitable solvent for the spectrochem. investigation of a series of compds. cannot be given. A critical expt. must be made in each case. If one excepts those cases where the process of soln. is not complicated by dissociation, rearrangement, salt formation, hydrolysis and other secondary processes, the spectrochem. values detd. in soln. may, with suitable control detns., be of value in the detn. of the constitution of the compds. in soln. Such detns. should be carried out with a concn. of at least 10%. The following new compds. were studied: *1,4-Dihydroxynaphthalene diethyl ether*, thick, reddish brown oil, b₁ 224-8°. *1,5-Derivative*, glistening leaflets, m. 96°. *1,4-Tetraethyl-diaminonaphthalene*, leaflets, m. 47-8°. *1,5-Derivative*, needles, m. 41°; *1,8-derivative*, m. 31-2°; *2,3-derivative*, leaflets, m. 75-6°; *2,6-derivative*, pale yellowish green needles, m. 69-70°; *2,7-derivative*, thick oil, b₁₅ 234-6°. *1-Keto-1,2,3,4-tetrahydro-7-methylnaphthalene*, thick crystals, m. 32.5-3.5°. *Tetraethyl-o-phenylenediamine*, b₁₀ 119.2-9.6°; *n-derivative*, b₁ 147.8-8.4°. *9-Methylanthrane*, yellowish green needles, m. 79-80°. *9-Ethyl derivative* m. 59°; *9-isocumyl derivative* m. 61°. *9-Ethylhydronitranol*, from anthrone and EtMgBr , m. 78°. In a vacuum over H_2SO_4 it loses H_2O , forming 9-ethylanthrane. *9-Ethyl-10-chloroanthracene*, yellowish green needles, m. 111°.

C. J. WEST

α -Naphthylnitramine and its rearrangements. E. BAMBERGER. *Ber.* 55B, 3383-92(1922).— α -Naphthylnitramine (A) (*Ber.* 27, 683(1894)) is unlike other (non-chromophoric) aryl nitramines in its gold-yellow color and in 2 reactions; (1) it gives with mineral acids $\alpha,\beta\text{-C}_{10}\text{H}_6(\text{NH}_2)\text{NO}_2$, but in alk. soln. it is isomerized through the intermediate stage of (salts of) α -diazonaphthalenic acid (B), $\text{C}_{10}\text{H}_7\text{N:N}(\text{O})\text{OH}$, to β -naphthoquinone- α -diazide (C), $\text{C}_{10}\text{H}_6(\text{O})(\text{N}_2)$, an anhydride of β -hydroxy- α -diazonaphthalene (D), $\text{C}_{10}\text{H}_6(\text{OH})(\text{N}_2)\text{OH}$; B and C appear also to be formed simultaneously by oxidation of diazo- α -naphthylamine with $\text{K}_2\text{Fe}(\text{CN})_6$. Diazo- β -naphthylamine (E) with $\text{K}_2\text{Fe}(\text{CN})_6$ gives the corresponding β -diazonaphthalenic acid (F) and α -naphthoquinonedia-

zide (G), but F is not transformed into G as is B into C. The peculiar action of A may be due to the smaller affinity factor of B, in comparison with F. It is probable that the salts of B are considerably hydrolyzed in soln., and that the non-ionized mols. are the source of D and C. The transformation of A to D is remarkably rapid. D as well as C gives an intense violet-red with resorcinol (delicate qual. test for A), whereas β -naphthyl- or other arylnitramines do not react. (2) The second peculiar reaction is the formation not of α - but of β -naphthol (H) on reduction of A with Na-Hg in alk. soln.; C is first formed as in reaction series (1), and is then reduced directly to H. The yellow color of A may be due to a minute amt. of C. 10 g. α -C₁₀H₇NH₂ (I) is melted in a mortar standing in hot H₂O, treated with 45 cc. concd. HCl while stirring, then slowly with 4.8 g. NaNO₃ in 50 cc. H₂O at -4°; at this temp. the soln. is run slowly with good stirring into a fresh soln. of 100 g. pulverized K₂Fe(CN)₆ and 55 g. KOH in 300 cc. H₂O, also well cooled; the mixt. must not foam, nor the temp. exceed -4°. After 14 hrs. standing at 0° (test for completion with R-salt) the mixt. is well agitated, filtered, and the soln. allowed to stand darkened for 24 hrs. when amber-yellow or yellow-red crystals of C are filtered off; careful addn. of H₂SO₄ to the filtrate at 0-10° soon ppts. gold-yellow crystals of A, which are washed with ice-H₂O and dried on tile; yield, 1.8-2 g.; m. 123-4°, explodes at higher temps., gradually darkens in sunlight, crystals from hot H₂O in small flat needles, is sol. in most org. solvents, decomps. somewhat in any solvent at the b. p.; its color survives crystn. and treatment with charcoal. When 50 g. instead of 55 g. KOH is used, traces of α -naphthylferrocyanic acid, of I, and of α,α' -azonaphthalene appear to be formed (imperfectly identified). An AcOH soln. of A stirred with a Zn rod is colored violet (reduction to diazonium salt). The cryst. Ag, and the Pb, salts of B are noted. 5 g. A in MeOH was treated with the calcd. amt. of MeONa and a small excess of MeI, and let stand 1-2 weeks; after distn. of MeOH the soln. was poured into an alkali soln. and extd. with Et₂O, yielding *N*-methyl- α -naphthylnitramine, a dark oil slowly solidifying to glassy, hard, shining, almost colorless crystals, m. 54.5-55°, crystd. several times from hot ligroin. 1 g. A in 12 cc. AcOH was treated with 5 drops concd. H₂SO₄ and, after standing darkened for 3 hrs., was poured on to ice, and filtered; distn. with steam superheated to 180° produced crystals of *1*-amino-2-nitronaphthalene (Ber 19, 802(1886)), which after crystn. from EtOH formed compact prisms of K₂Cr₂O₇-color, with greenish cast, m. 143°. Boiling with KOH in H₂O substitutes OH for NH₂; reduction with Zn dust and dil. H₂SO₄ forms *1,2*-diaminonaphthalene. 2 g. A was dissolved in 20 cc. (45% excess) of N NaOH and 300 cc. H₂O and at once extd. 7 times with 30-40 cc. Et₂O, which on evapn. yielded 0.95 g. C in sheaves of shining golden-yellow needles, m. 94-4.5°; a somewhat lower yield of less pure material is obtained with the calcd. amt. of NaOH; 0.4 g. A was recovered by cooling the acidified filtrate. 2 g. A suspended in 100 cc. H₂O and treated while cooling with 12 g. 4% Na-Hg formed at first a light yellow, finally almost black soln. and some tar; from the latter, steam distn. removed pure C₁₀H₈. Et₂O extn. of the alk. soln. gave a dark blue mass from which, after treatment with dil. HCl, were sepd. H and I; HCl pptd. from the exhausted alk. soln. a red resin from which steam distn. removed pure H; NH₃ was also formed; aminonaphthol was not found. 1 g. A in AcOH was treated with the calcd. amt. of NaNO₂ soln., dild. with H₂O, and acidified with HCl, unchanged A was removed with Et₂O, and NaOH driven out with air; when poured into alk. H soln., the H₂O layer from the Et₂O extn. ppts. red α -naphthylazo- β -naphthol, which after several crystns. from boiling xylene and finally from AmOH forms diamond-like needles with grass-green surface sheen, m. 228-9°, proving reduction of A to the α -naphthylidiazonium salt by the HNO₂.

A. R. ALBRIGHT

Influence of substitution in the components upon the equilibrium of binary solutions. XXXVI. The equilibria of dihydroxynaphthalenes with amines. ROBERT

KREMANN, FRANZ HEMMELMAYR AND HEINRICH RIEMER. *Monatsh.* 43, 164–208 (1922); cf. *C. A.* 16, 560.—1,4- $C_{10}H_8(OH)_2$ (A) forms with β - $C_{10}H_7NH_2$ (B) an equimol. compound, m. 143°, which forms eutectics with A at 125° (36% B) and with B at 96° (76% B). 1,5- $C_{10}H_8(OH)_2$ (C) gives with B an equimol. compound, m. 229.5°, which forms eutectics with C at 212° (35% B) and with B at 107° (95% B). 1,6- $C_{10}H_8(OH)_2$ (D) and B form a compound (2 D : 3 B), m. 110.5°, which forms eutectics with D at 92° (65% B), and with B at 96° (65% B). 1,8- $C_{10}H_8(OH)_2$ (E) and B form an equimol. compound, m. 124°, which forms eutectics with E at 75° (38% B), and with B at 76° (55% B). 2,3- $C_{10}H_8(OH)_2$ (F) and B form an equimol. compound, m. 168°, which forms eutectics with F at 145° (24% B), and with B at 106.5° (97% B). 2,6- $C_{10}H_8(OH)_2$ (G) and B give a compound (1 G and 2 B), m. 171.5°, which forms eutectics with G at 165° (41% B) and with B at 109° (98% B). 2,7- $C_{10}H_8(OH)_2$ (H) and B give an equimol. compound, m. 163°, which forms eutectics with H at 153° (36% B) and with B at 108° (98.5% B). C and α - $C_{10}H_7NH_2$ (I) give a eutectic at 44° (95% I); G and I at 46° (98% I); H and I at 35° (91% I). A and I give an equimol. compound, m. 143°, which forms eutectics with A at 129° (39% I) and with I at 44° (94% I). D and I give a compound (2 D : 3 I), m. 84.5°, which forms eutectics with D at 76° (53% I) and with I at 43° (92.5% I). E and I give an equimol. compound, m. 76.5°, which forms eutectics with D at 74° (45% I) and with I at 41° (84% I). F and I give a compound (2 F : 3 I), m. 103°, which forms eutectics with F at 97° (54.5% I) and with I at 35° (87% I). D and p - $C_6H_4(NH_2)_2$ (J) give an equimol. compound, m. 170°, which forms eutectics with F at 141° (4% J) and with J at 125° (95% J). E and J form a compound (2 mols. E : 1 mol. J), m. 118°, which gives eutectics with E at 109° (21% J) and with J at 106° (37% J). F and J form a compound (2 F : 1 J), m. 164°, which gives eutectics with F at 141° (4% J) and with J at 118° (70% J). G and J give an equimol. compound, m. 212°, which forms eutectics with G at 195° (10% J) and with J at 140° (95% J). H and J form a compound (2 H : 1 J), m. 180°, which forms eutectics with H at 171° (10.5% J) and with J at 129° (81% J). A and m - $C_6H_4(NH_2)_2$ (K) give an equimol. compound, m. 124°, which forms a eutectic with K at 55° (92.5% K). D and K give an equimol. compound, m. 125°, which forms eutectics with D at 87° (22% K) and with K at 49° (89% K). E and K form an equimol. compd., m. 101°, which forms eutectics with E at 75° (32% K) and with K at 58° (92% K). F and K form an equimol. compound, m. 149°, which forms eutectics with F at 122° (24% K) and with K at 53° (94% K). G and K form an equimol. compound, m. 171°, which forms eutectics with G at 125° (35% K) and with K at 61° (98% K). H and K form an equimol. compound, m. 139°, which forms eutectics with H at 126° (33% K) and with K at 53° (98% K). The system A - o - $C_6H_4(NH_2)_2$ (L) has a eutectic at 87° (83% L). F and L form a eutectic at 96° (93% L). The formation of a compd. in these cases was not proven. D and L give an equimol. compound, m. 95°, which forms eutectics with D at 76° (32% L) and with L at 62° (61% L). E and L give an equimol. compound, m. 151°, which forms eutectics with E at 117° (7% L) and with L at 93° (85% L). G and L give a compound (2 G : 3 L), m. 150°, which forms eutectics with G at 124° (30% L) and with L at 99° (92% L). H and L give a compound (2 H : 3 L), m. 140°, which forms eutectics with H at 101° (38% L) and with L at 96° (91% L). A and $BzNH_2$ (M) give a eutectic at 91° (61.5% M). C and M form a eutectic at 106° (72% M). D and M form a eutectic at 90° (45% M). E and M form a eutectic at 46° (46% M). G and M form a eutectic at 87° (48% M). H and M form a eutectic at 78° (52% M). F and M form a compound (1 F : 3 M), m. 113°, which gives eutectics with F at 80° (48% M) and with M at 106° (75% M).

C. J. WEST

Influence of substituents in the components on the equilibrium in binary solutions. XXXVIII. The binary systems of the three isomeric phenylenediamines with trinitro-

benzene and trinitrotoluene. ROBERT KREMAN and OTTO MAUERMANN. *Monatsh.* 43, 315–30 (1923); cf. *C. A.* 17, 275.—1,3,5- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ (A) forms a compd. with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ (B) which contains 33.7% B and m. 163° ; the eutectic of this compd. with B lies at 92° and 93% B, with A at 108° and 3% B. The compd. of A and $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ (C) contains 33.7% C and m. 168° ; its eutectic with A lies at 105° and 7% C, with C at 45° and 82% C. The compd. of A and $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ (D) also contains 33.7% D and m. 145.5° ; the eutectic with A lies at 101.5° and 9% D, with D at 106° and 64% D. 1,2,4,6- $\text{Me}_4\text{C}_6\text{H}_2(\text{NO}_2)_2$ (E) and B form a compd. contg. 32.3% B and m. 97.5° ; the eutectic with B lies at 83° and 57% B, with E at 65° and 9% B; the compd. of E and C m. 105° and contains 32.3% C; the eutectic with C lies at 57.5° and 90.5% C, with E at 70° and 6% C. The compd. of E and D m. 93° and contains 32.3% D; the eutectic with D lies at 88° and 38% D, with E at 64° and 8% D. XXXIX. Several binary systems of triphenylmethane, triphenylcarbinol and trimethylcarbinol with other components. R. KREMAN, O. MAUERMANN, ROBERT MÜLLER II, and WILHELM RÖSLER. *Ibid.* 321–33; cf. *C. A.* 16, 89.— Ph_3CH and $m\text{-C}_6\text{H}_4(\text{NH}_2)_2$ form a eutectic at 58° and 4% Ph_3CH (former results gave 60° and 3.5% Ph_3CH), while the eutectic with $\text{o-C}_6\text{H}_4(\text{NH}_2)_2$ lies at 76.5° and contains 12.5% Ph_3CH . Ph_3CH and 1,2,4- $\text{C}_6\text{H}_3(\text{NO}_2)_3$ do not form a compd. but the eutectic lies at 81° with 86% Ph_3CH . Ph_3CH and Ph_3COH form a simple eutectic at 78° and 17% Ph_3COH . Me_3COH and the three $\text{HOC}_6\text{H}_4\text{NO}_2$ form compds. contg. $2\text{Me}_3\text{COH}$ to 1 $\text{HOC}_6\text{H}_4\text{NO}_2$. The eutectic points with the o-deriv. lie at 11° and 31° , with the $m\text{-deriv.}$ at 1° and 28° and with the $p\text{-deriv.}$ at 7° and 28° . Ph_3COH and 1,2,4- $\text{HOC}_6\text{H}_3(\text{NO}_2)_3$ form a simple eutectic at 100.5° and 19% Ph_3COH . Me_3COH forms an equimol. compd. whose eutectic with $\text{HOC}_6\text{H}_3(\text{NO}_2)_3$ lies at 85° and 17% Me_3COH and with Me_3COH at 20° and 97% Me_3COH . C_6H_6 forms a simple eutectic with Me_3COH at 19° and 95% Me_3COH and with Ph_3COH at 69° and 30% Ph_3COH . XL. Binary solution equilibrium of acid amides with acid anhydrides and acids. R. KREMAN, O. MAUERMANN and VICTOR OSWALD. *Ibid.* 335–43.—The temp. of the primary crystn. of an equimol. mixt. of AcNH_2 and Bz_2O , after careful melting, is 84° . This compd. forms a eutectic with Bz_2O at 78° and 25% Bz_2O and with AcNH_2 at 36° and 93% Bz_2O . The system $\text{BzNH}_2\text{-Bz}_2\text{O}$ forms a eutectic at 37° and about 91–92% Bz_2O . The curves for $\text{BzNH}_2\text{-Ac}_2\text{O}$ and $\text{AcNH}_2\text{-Ac}_2\text{O}$ were continuous between 0 and 90 mol. % Ac_2O . AcNH_2 and AcOH form an equimol. compd., m. 5.5° , which forms a eutectic with AcOH at -16.5° and 69.5% AcOH . BzNH_2 and BzOH form a eutectic at 78° ; BzNH_2 and AcOH form a eutectic at -2° and 73% AcOH , while that of AcNH_2 and BzOH lies at 38° and 56% BzOH .

C. J. WEST

Synthesis of perylene from 1,12-dihydroxyperylen. ALOIS ZINKE and RUPERT DENG. *Monatsh.* 43, 125–8 (1922).—1,12-Dihydroxyperylen (A) is obtained by heating an intimate mixt. of $(\text{C}_{10}\text{H}_7\text{OMe})_2$ with 4 parts anhyd. AlCl_3 an hr. at $140\text{--}50^\circ$; the dibenzoate forms brownish yellow amorphous flocks, decomp. about 224° . Distn. of A with Zn dust readily reduces it to perylene.

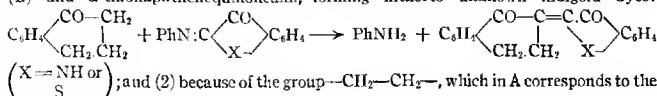
C. J. WEST

Nitration of 3-chloroacenaphthene. GLADYS FARNELL. *J. Chem. Soc.* 123, 60–1 (1923).—The nitration of 3-chloroacenaphthene in AcOH-HNO_3 gives, after repeated crystn. from EtOH , a compd. m. $160\text{--}6^\circ$ (probably a mono- NO_2 deriv.) and 3-chloro-4-nitroacenaphthene (A), m. $136\text{--}8^\circ$. The 4-amino derivative forms fine needles and m. 145° . On reduction of A with H and Pd, the known 3- NH_2 deriv. is obtained (Graebe, *Ann.* 327, 81 (1903)); oxidation with CrO_3 gives the chloronitronaphthalic acid, yellow powder; crystd. from AcOH , it gives pale yellow, shining leaflets of the anhydride. Sodium, calcium, barium salts.

C. J. WEST

Dyestuff derivatives of α -ketotetrahydronaphthalene (α -tetralone). WALTER HERZOG and J. KREIDL. *Ber.* 55B, 3394–400 (1922).— α -Ketotetrahydronaphthalene

(A) is of interest for the synthesis of indigoid dyes because (1) of the reactive H atoms of the $-\text{CH}_2-$ group adjacent to the $-\text{CO}-$, which make possible reactions with the α -anilides (or α -halogen compds.) of cyclic o -diketones such as α -isatinanil (B) and α -thionaphthenequinoneanil, forming hitherto unknown indigoid dyes:



NH group of indoxyl. Of the various naphthalene-indigos, 2-naphthalene-2'-indole-indigo (D) from α -naphthol and B, is extraordinarily similar in shade to indigo (E); it differs mainly in its higher sol. in org. solvents. 2-Tetrahydronaphthalene-2'-indoleindigo (F) and 2-tetrahydronaphthalene-2'-thionaphtheneindigo (G) are almost identical in shade with, resp., E, and 2-indole-2'-thionaphtheneindigo (H); F and G vat with remarkable ease, and are more sol. in org. solvents. A has become more readily available through Schröter's process (D. R. P. 346,948, 352,720) of CrO_3 oxidation of tetrahydronaphthalene, or catalytic reduction of α -naphthol. β -Isatinanilide does not couple with A to the corresponding indirubin deriv. Condensation of 2 mols. A with dialdehydes such as terephthalic aldehyde (I) gave colored compds. but no dyes; reaction between 1 mol. each of A, I, and 3-ketothionaphthene (J) formed a substance of uncertain structure, not a dye, and not of the compn. $\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CO.C:CHC}_6\text{H}_4\text{CH:C.CO.C}_6\text{H}_4\text{S}$;

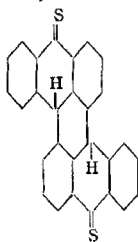
and in smaller amt. a *dyesstuff* (K), probably $\text{C}_6\text{H}_4(\text{CH:C.CO.C}_6\text{H}_4\text{S})_2$ (C. A. 8, 2889;

D. R. P. 239,916; C. A. 6, 2177). Equiv. amts., 1.5 g. A and 2.2 g. B, were dissolved in 15 cc. petroleum (b. 150–200°) and heated 1 hr. under a reflux; the color goes from cherry-red to blue-violet, and crystals of crude F sep. on cooling; it is extd. several times with a little warm MeOH until the solvent becomes clear blue, and is then crystd. from EtOH, forming blue-violet, bronzy crystals decomp. at about 250° with partial sublimation. F is sol. in cold concd. H_2SO_4 with greenish blue color, and repts. in flocks, on diln.; in fuming H_2SO_4 it gives a blue-violet color, and forms a stable, pure blue sulfonic acid. F is fairly stable toward cold dil. caustic alkali or carbonate, but is attacked at higher temps.; it gives a yellow vat with alk. $\text{Na}_2\text{S}_2\text{O}_4$, from which it seps. as a greenish substance with bluish bloom; it dyes wool or cotton a pure blue. Equiv. amts. of A (1.5 g.) and C (2.3 g.) in 7 g. Ac_2O were heated 2 hrs. under a reflux, the yellowish red color changing to garnet; on cooling and washing with cold MeOH, G was obtained perfectly pure in small red-violet bronzy needles; in its reactions with acids and alkalies it is similar to F; it dyes wool a brown-violet; cotton, beautiful red-violet shades of moderate fastness. 1.34 g. I and 3 g. A (2 mols.) in 10 cc. warm EtOH on treatment with a few drops of 25% NaOH deposited on cooling an abundant cryst. ppt. from the strongly colored soln.; the straw-yellow product from 2 crystals from AcOH turns brown at 230°, m. gradually 240–55°; diln. of a concd. H_2SO_4 soln. ppts. yellow flocks; the compd. does not form a vat. A mixt. of 1.15 g. A, 1.5 g. J, and 1.35 g. I, 1 mol. each, in 25 cc. warm EtOH treated with a few drops concd. alkali and warmed a short time on a H_2O bath pptd. an orange-red cryst. compd. which was washed with a little MeOH and extd. with boiling EtOH, from which, on cooling, golden yellow matted needles, m. 192–3°, sepd.; the product is sol. in concd. H_2SO_4 with greenish blue color, and reprecip. by H_2O , rapidly decompd. by warm alkalies, has none of the properties of a vat dye; its constitution is uncertain. The smaller portion, insol. in EtOH, gave glistening orange-red needles from xylene, with bluish green color in cold concd. H_2SO_4 , and forming a sulfonic acid with warm fuming H_2SO_4 . The *dyesstuff* K is fairly stable toward alkali, and slowly forms a vat with alk. $\text{Na}_2\text{S}_2\text{O}_4$. Many other cyclic compds. with the grouping

—CO—CH₂— react with A and I. Equiv. amts. of A and PhCH:CHCHO in alc. treated with a little NaOH produce β -cinnamylidene- α -tetralone, m. 132–4°, large yellow leaves from MeOH, sol. in concd. H₂SO₄ with yellowish red color, and forming a resinous polymer at 220–30°.

A. R. ALBRIGHT

meso-Thioanthracene derivatives. I. Observations on the production of dithioanthraquinone, dithiodianthrone and other closely related derivatives. I. M. HILBRON AND J. S. HEAYON. *J. Chem. Soc.* 123, 173–85(1923).—Attempts were made to prep. *meso*-dithioanthracene starting from 9,10-Cl₂C₁₄H₈ or the Br deriv., but with neither Na₂S nor NaHS could more than the merest trace of any S-contg. compd. be obtained. The halogen atoms in the 9,10-position can be replaced by S since *dithioanthraquinyl diphenyl ether*, bright yellow needles, m. 212°, results upon heating the above Br deriv. with PhSH and C₆H₁₁N for 6 hrs. at 180° under pressure. It is not hydrolyzed on heating with alkali or concd. HCl. With fuming HNO₃ it yields C₁₄H₈O₂. The use of solvents was then tried. EtONa in EtOH was completely satd. with dry H₂S and 9,10-Cl₂C₁₄H₈, finely powdered, added, the stream of H₂S being continued 0.5 hr. after the addn. No reaction occurred at room temp. but after heating 2 hrs. at 120°, about 0.5 of the Cl compd. was recovered, some C₁₄H₈O₂ was isolated, while the alc. mother-liquor contained anthranol and anthrone and a very small amt. of a S-contg. substance, m. 207°. Using AmOH in place of EtOH, *dithioheptacyclene* (A),



was obtained as small yellow crystals from PhNO₂, m. 320°. The course of the reaction can generally be followed by the color change from yellow to bright red towards the end of the reaction. In the 1st expt., *dithioanthraquinone*, small ruby-red crystals, m. 176°, was believed to have been isolated, but in later expts. only minute quantities could be found. It rapidly decomps. in air, SO₂ being evolved. After removal of A from the AmOH, *bisthioanthrone disulfide* 1st seps. as very characteristic bright golden yellow needles, m. 194°, and then *dithiodianthrone*, dark red prisms, m. 202°. In 1 case, *dianthranyl sulfide* was isolated as bright red crystals, m. 174–6°. Reduction with Zn dust gave C₁₄H₁₀. Another product isolated in only 1 expt. was *bisanthrone sulfide*, flaky, yellowish brown crystals, m. 185°.

C. J. WEST

Anemonins. YASUHIKO ASAHINA AND ATSUSHI FUJITA. *Acta Phytotchim.* 1, 1–42(1922).—A resumé in German of Asahina's work on anemonin, most of which has been published in Japanese only (cf. Beckurts, *Arch. Pharm.* 230, 182–206); Meyer, *Monatsh.* 17, 283–99(1896); 20, 634–46(1899); (*C. A.* 8, 1780; 9, 1482; 10, 1520; 13, 2517; 14, 1318, 1384, 3227; 15, 2439).

J. C. S.

Pyroles. IV. Pyrrolealdehyde (II) and pyrrolenitrile. HANS FISCHER AND WERNER ZERWECK. *Ber.* 56B, 519–27(1923); cf. *C. A.* 17, 759.—While the reaction of HCN with trimethylpyrrole does not proceed in Et₂O, in CHCl₃ a 66% yield of 2,4,5-trimethylpyrrolealdehyde (A), reddish crystals, m. 141°, is obtained. The reaction with Ehrlich's reagent is negative in the cold, strongly positive on heating. *Phenylhydrazone*, compact, brownish crystals, m. 138°; *oxime*, needles, m. 164°; *semicarbazone*,

compact crystals, m. 198°; *aldazine*, m. 273°; *azlactone*, $C_{11}H_{10}O_2N_2$, reddish brown needles, m. 198°; heated with 1% NaOH this gives *2,4,5-trimethylpyrrole-3-benzoyl-aminoacrylic acid*, m. 178° (decompn.). The *rhodanine condensation product* is brownish red and m. 286°. The yield of *2,4-dimethyl-5-formylpyrrole* (B), prepd. as above, is 92%. Sapon. of *2,4,5-trimethyl-3-cyanoacetylpyrrole* did not give the expected keto acid but the 3-Ac deriv. *2,5-Dimethyl-3-carbethoxy-4-formylpyrrole oxime*, m. 223° (decompn.), gave the *4-cyano derivative*, glistening needles, m. 152°, when heated with Ac_2O for 0.5 hr. The corresponding *5-cyano derivative* m. 159°. *2,4,5-Trimethyl-3-cyanopyrrole*, m. 140°. Attempts to reduce these aldehydes resulted in the formation of the corresponding di- or trimethylpyrroles, the CHO group being split off. Heated in a sealed tube with $EtONa$ for 7 hrs. at 160°, A gives *2,3,4,5-tetramethylpyrrole*, analyzed as the *picrate*, compact yellow crystals, m. 130°. A is very resistant to the action of alkalis; heating with aq. or alc. 20% NaOH for 6 hrs. did not change it. In the case of *2,4-dimethyl-3-carbethoxy-5-formylpyrrole*, the corresponding *3-carboxylic acid*, m. 283-4° (decompn.), was obtained. *2,5-Dimethyl-4-formylpyrrole-3-carboxylic acid*, needles, m. 248°. B, heated a few min. with concd. HCl, gave bis-[*2,4-dimethylpyrrol*]-methene, m. 118°. Bis-[*2,4-dimethyl-3-carbethoxypyrryl*]-methene, $C_{18}H_{20}O_4N_2$, dark red long needles, m. 190°. *2,4,5-Trimethyl-3-(dimethylaminoacetyl)pyrrole hydrochloride*, by the action of Me_3NI in EtOH upon the 3- $ClCH_2CO$ deriv., m. 248°. The free amine, m. 130°. The corresponding *phthalimido derivative*, m. 227°. C. J. WEST

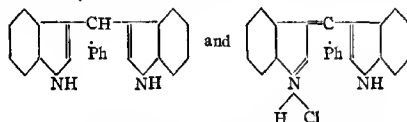
Graphite from pyrrole and from thiophene. Preliminary note. R. CRUSA. *Gazz. chim. ital.* 52, II, 130-1 (1922).—C. previously expressed the opinion (*Atti accad. Lincei* 30, I, 73, 468) based on the existence of satd. complexes C_6 , C_4NH , C_4S , that such compds. should have a tendency to polymerize, giving graphitic (C_4NH) $_n$, (C_4S) $_n$, i. e., *graphite of pyrrole* and of *thiophene*. Tetraiodopyrrole heated at 150-200° gave (C_4NI) $_n$. Heated at higher temps. (C_4NH) $_n$ was obtained as black scales resembling graphite. C_4IS heated similarly first eliminated 3 atoms of I at 450°. The 4th atom of I was eliminated by heating again in an inert gas at incipient red heat. The product was approx. (C_4S) $_n$ and is thiophene graphite. Pauly (C. A. 8, 127) obtained (C_4NI) $_n$ first from tetraiodimidazole and then (C_4N_2) $_n$ the *graphite of imidazole*. In all 3 cases 3 atoms I were eliminated at first and the 4th only at higher temps. C. then prepd. *tetraiodofuran*, m. 145°. At 160° it begins to evolve I and at 202° decomps., leaving a black residue resembling the other graphites. The expts. are to be continued.

E. J. WITZERMANN

Catalytic hydrogenation of alkyl-substituted pyrrole azo dyestuffs. I. HANS FISCHER AND FRIEDRICH ROTHWEILER. *Ber.* 56B, 512-9 (1923).—The reduction of the pyrrole azo dyestuffs in alk. soln. leads to the formation of amines. In alc., the reduction proceeds only to the hydrazo step. In alk. soln., the 1st step (hydrazo) proceeds rapidly but the 2nd step (amine) is very slow. *2,4,5-Trimethylpyrrole-3-azobenzenesulfonic acid* is reduced by shaking for 12 hrs. with H and Pt black to *2,4,5-trimethyl-3-aminopyrrole*, m. 186°. *Hydrochloride*, rhombic prisms, m. 234° (decompn.). *Picrate*, decomps. 210-30°. *2,4-Dimethyl-3-acetyl-5-aminopyrrole*, m. 223° (decompn.). *Picrate*, m. 175-90°. *2,5-Dimethyl-3-carbethoxy-4-aminopyrrole hydrochloride*, rectangular leaflets from HCl, fine needles from EtOH, m. 212° (decompn.). The free base is oily. *Picrate*, m. 185-95°. III does not appear to decomp. this amine. *2,4-Dimethyl-3-acetylpyrrole-5-azobenzenesulfonic acid* is obtained in nearly quant. yield by the interaction of the 5- CO_2H deriv. and $HO_2SC_6H_4N_2X$. *p-O_2NC_6H_4N_2X gives the *5-p-nitroazobenzene derivative*, orange, m. 198° (decompn.). *2,4-Dimethyl-3-carbethoxy-5-azobenzene pyrrole*, small yellow needles, m. 127°. *Picrate*, m. 156-8° (decompn.). *Styphnate*, m. 163°. C. J. WEST*

Syntheses in the indole group. II. The influence of the solvent on the Grignard

reaction. RIKO MAJIMA AND MUNIO KOTAKE. *Ber.* 55B, 3865-72(1922).—In the following outline the substances reacting with indolylmagnesium iodide, the product of the reaction and the yields in Et₂O and anisole soln. expressed in % of the theoretical, are given: (1) HCO₂Et, β -indole-aldehyde, trace, 33; (2) CO₂, β -indolecarboxylic acid, 8.6, 25; (3) Me₂CO, β -indolylidimethylmethane, 22.5, 30.4; (4) BzH, β -di-indolylphenylmethane (A), 20, 61.6; (5) ClCO₂Et, Et β -indolecarboxylate, 53.5, 38.7; (6) MeCOCl, β -indolyl Me ketone, 93, 61; (7) CH₂ClCOCl, β -indolyl chloromethyl ketone (B), 45, 4.8. These results indicate that the action of compds. contg. the C:O group on indolylmagnesium iodide gives better yields in anisole than in Et₂O solns., while with acid chlorides the Et₂O is preferable. The expts. were carried out by dropping a dry Et₂O soln. of the reacting substance on a cooled Et₂O soln. of indolylmagnesium iodide, decomp. the product formed with H₂O, acidifying with AcOH and extg. with Et₂O. In expt. 2 the dry CO₂ was led into the Et₂O soln. Using the same substances shown in the outline Oddo obtained as the reaction products in 2 *N*-indolecarboxylic acid and, in 5 Et α -indolecarboxylate. A is easily sol. in MeOH, Et₂O, CHCl₃, AcOH and PhNO₂, seps. from ligroin in amorphous form, from warm alc. or C₆H₆ as crystals. The crystals, m_p 120-1°, from C₆H₆ have 0.5 mol. of C₆H₆ of crystn. which is lost when the crystals are dried under diminished pressure in a PhMe bath, when they turn yellow and m. 149-52°. The hydrochloride of A, red, short prisms from CHCl₃, m. 245-8°, is obtained by oxidation with FeCl₃ in alc. It is the simplest "rosindole" dye. The action of MeMgI on A in Am₂O causes the liberation of CH₄ in a vol. indicating the presence of 2 free imino H atoms and indicates that the methane C is not combined to N. The formulas for A and its hydrochloride are:



B, from Et₂O or CHCl₃, forms crystals m. 212-4°; small rhombic crystals from alc., easily sol. in Me₂CO and AcOEt, difficultly sol. in C₆H₆, ligroin, Et₂O, anisole and phenetole.

G. W. STRATTON

Some derivatives of indolinone. OLDRIK TOMICEK. *Chem. Listy* 16, 1-4, 35-9 (1922).—Brunner's reaction whereby indolinones are prepd. from the phenylhydrazides of fatty acids (*Monatsh.* 17, 253-81(1896); 18, 527-49(1897)), is tried with the phenylhydrazides of β -phenylpropionic acid, and found to give good yields. By its means, a number of benzylindolinones were prepd. Phenylpropionylphenylhydrazine was converted into 3-benzyl-2-indolinone, m. 132°. Its *l*-acetyl deriv., m. 82°, was prepd., also the 5,7-dibromo deriv., m. 194°. 3-Benzyl-1-methyl-2-indolinone, m. 95-6°, was prepd. by the Brunner reaction from phenylpropionylphenylmethylhydrazine, m. 102°, obtained from PhMeNNH₂. 3-Benzyl-7-methyl-2-indolinone, m. 196°, was prepd. from phenylpropionyl-*o*-tolylhydrazine, m. 122°. Its monobromo deriv., m. 191°. 3-Benzyl-5-methyl-2-indolinone, m. 149.5°, was prepd. from phenylpropionyl-*p*-tolylhydrazine, m. 120°. Its monobromo deriv., m. 198°, was also obtained. 3-Benzyl-*q*(or 6)-methyl-2-indolinone, m. 209°, was obtained from phenylpropionyl-*m*-tolylhydrazine, m. 125°. It was expected that a mixt. of the 4- and 6-Me derivs. would be formed, but only one product was obtained; which of the two it is, it is not yet possible to state with certainty.

J. C. S.

The action of nitrobenzene on the sodium and potassium derivatives of carbazole. GUILLAUME AND MARCEL DE MONTMOLLIN. *Helvetica Chim. Acta* 6, 94-101(1923).—*p*-Nitrophenylcarbazole (B), prepd. by melting 25 g. carbazole (A) with 1 equiv. of KOH,

cooling, pulverizing, adding to 300 g. PhNO_2 , raising the temp. slowly to $45-50^\circ$, keeping at this temp. for several hrs. and then removing the excess of PhNO_2 with steam, seps. in yellow crystals from PhH or AcOH , m. 212° , fairly sol. in PhH , AcOH , PhNO_2 or PhNH_3 , slightly sol. in EtOH and insol. in H_2O . The reaction is: $\text{C}_{12}\text{H}_8\text{NK} + \text{PhNO}_2 + \text{O} \longrightarrow \text{C}_{12}\text{H}_8\text{NC}_6\text{H}_5\text{NO}_2 + \text{KOH}$, the O being furnished by the excess of PhNO_2 . *p*-Aminophenylcarbazole (C), prepd. by reducing B with Fe and HCl in EtOH , boiling until colorless, neutralizing with Na_2CO_3 , filtering and concg. the filtrate, forms a resinous substance which was converted into the following cryst. derivs.: *picrate*, m. 200° (decompn.); *acetyl derivative* (D), from EtOH , m. 257° ; *p*-phthalaminophenylcarbazole, by fusion of C and $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$, crystals from PhH , m. 210° ; $\text{C}_{12}\text{H}_8\text{NK}$ on heating with *m*-bromophthalanil gave a low yield of *m*-phthalaminophenylcarbazole, m. 216° . The *diazonium chloride*, *sulfate*, and *nitrate* of C were prepd. in the usual manner and coupled with $\beta\text{-C}_{10}\text{H}_7\text{OH}$ in alk. soln., yielding *β -naphtholazophenylcarbazole*, crystals from xylene, m. 230° ; the *diazonium sulfate* on continued boiling with EtOH gives *phenylcarbazole*, m. 88° (cf. D.R.P. 224951). *p*-Chlorophenylcarbazole, prepd. by the Sandmeyer reaction from the *diazonium chloride* or by heating $\text{C}_{12}\text{H}_8\text{NK}$ with $p\text{-ClC}_6\text{H}_4\text{Br}$ to 210° , forms crystals from EtOH-PhH , m. 146° , which are sol. in PhH , slightly sol. in EtOH and insol. in H_2O . *p*-Cyanophenylcarbazole, prepd. by the Sandmeyer reaction, m. 165° . *Azophenylcarbazole*, prepd. by reduction of B with Zn and a small amt. of acid, forms crystals from $\text{C}_6\text{H}_5\text{N}$ or PhNO_2 , m. 277° . B is decompd. by concd. H_2SO_4 but may be sulfonated by suspending in PhNO_2 and treating with a mixt. of H_2SO_4 and ClSO_3H ; this *sulfonic acid* yields on reduction an NH_2 compd., which was diazotized and coupled with $\beta\text{-C}_{10}\text{H}_7\text{OH}$. B in PhNO_2 with HNO_3 yields a *dinitrophenylcarbazole* which after recrystn. from $\text{PhNO}_2\text{-EtOH}$ m. 274° and is reduced by Fe in EtOH to the *diamino derivative*; the latter with Ac_2O gives a *diacetyl derivative*, m. 274° . D was similarly nitrated, yielding an *acetylaminophenyl*dinitrocarbazole (E), crystals from PhNO_2 , m. 234° ; E on hydrolysis gave *aminophenyl*dinitrocarbazole, crystals from EtOH , Me_2CO or $\text{EtOH-H}_2\text{O}$, m. 320° . *m*-Nitrotolylcarbazole, prepd. like B, m. 138° .

N. A. LANGE

Nitroso-*N*-hydroxyindazole. I. BAMBERGER. Ber. 55B, 3371-5(1922).—N-

Hydroxyindazole (A), $\text{C}_6\text{H}_4\text{N} \begin{array}{c} \diagup \text{N} \diagdown \\ | \quad | \\ \text{C} \quad \text{C} \end{array} \text{NOH}$, prepd. from *o*-azidobenzaldoxime (B) and

caustic alkali (Ber. 35, 54, 1885(1902)), when treated in acid soln. with NaNO_2 (Ann. 305, 344(1899)) gives red *nitroso-N-hydroxyindazole* (C), $\text{C}_6\text{H}_4\text{N} \begin{array}{c} \diagup \text{N} \diagdown \\ | \quad | \\ \text{C} \quad \text{C} \end{array} \text{NOH}$ (Ber. 33,

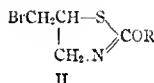
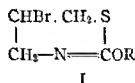


1783(1900); 35, 3886(1902); C. A. 4, 3222), and with Fe''' salts gives a violet-brown color and ppt.; *aci-nitroparaffins* (D) (Konowalow, Ber. 35, 1893) react in similar ways, but C has not necessarily the same structure as D, since its reactions are explicable in consideration of its mode of formation, and color; D on treatment with HNO_2 require preliminary neutralization with alkali, followed by acidification. Both C and its salts, which are also red, are probably C-NO compds. 0.055 g. C in AcOH was shaken with an excess of finely cut tin foil until the color, at first red, then yellow, became const. (1 hr.); the turbid soln., poured from the Sn residue, was allowed to evap., the solid taken up in dil. HCl, freed from Sn with H_2S , the filtrate concd., treated with NH_4OH , extd. with Et_2O , the solvent nearly all evapd. and the soln. treated with gasoline which pptd. white shining leaflets of *3-aminoindazole* (E) (Ann. 305, 346(1899)), m. $153-4^\circ$; an alk. soln. exposed to air is colored at once deep red, due to azoindazole which was isolated by pptn. with $\text{K}_2\text{Fe}(\text{CN})_6$; it gives a red soln. also with dil. HCl; HNO_2 ppts. the very slightly sol. *nitrate*, in dark Bordeaux-red needles with greenish cast; cautious

reduction with Zn dust and dil. HCl also gives E. It is possible that $C_6H_4(NHOH)CH:NOH$ also, on treatment with KOH, will give A as well as does B, from the analogy of the formation of anthranil (C. A. 12, 2570) from either $C_6H_4(NHOH)CHO$ or $C_6H_4(N_2)CHO$.

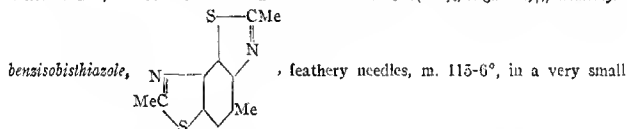
A. R. ALBRIGHT

Interaction of aliphatic alcohols and β,γ -dipropyl isothiocyanate. R. M. HANN. *J. Am. Chem. Soc.* 45, 482-6(1923).—By the action of aliphatic ales. ROH (R = Me, Et, Pr) on $BrCH_2CHBrCH_2NCS$ (A) Dixon obtained what he thought were 2-alkoxy-5-bromo-4,6-dihydro-1,3,4-thiazines (I), formed by elimination of HBr from the intermediate compds. $BrCH_2CHBrCH_2N:C(OR)SH$, while Gabriel concluded from oxidation expts. that D.'s compds. are 5-bromomethyl-2-alkoxy- Δ^4 -thiazolines (II). Desiring to obtain the higher homologs of I, H. treated A with BuOH, iso-BuOH and iso-AmOH and obtained in all 3 cases the same compound (B). Moreover, all 3 of D.'s compds. have about the same m. p. (95-7°) as B, and a repetition of his work with EtOH gave a product identical with B; the identity of the different preps. was established by analysis and crystallographic and optical examn. The most plausible assumption is that B is 5-bromomethyl-2-hydroxy- Δ^4 -thiazoline (II, R = H), formed by elimination of RBr from the intermediate $BrCH_2CHBrCH_2N:C(OH)SR$.



C. A. R.

Benzobisthiazoles. II. S. R. H. EDGE. *J. Chem. Soc.* 123, 153-6(1923); cf. C. A. 16, 2509.—In order to help in establishing the formula of the previously prepd. compd., which was considered as 2,6-dimethylbenzobisthiazole (A), a Me_2 deriv. has been prepd. The action of PS_2 upon $m-MeC_6H_3(NHAc)_2$ gave a mixt. of 7 mols. dithio- and 2 mols. monothio-deriv., minute, yellowish white needles, m. 178°. Repeated crystn. of this product from H_2O gave pure dithioacetyl-*m*-tolylendiamine, fine, yellowish white needles, m. 185-6°. Oxidized in NaOH with $K_2Fe(CN)_6$, it gave 2,4,7-trimethyl-



yield. *Hydrochloride*, microneedles, m. 170-80° (decomp.). MeI gave a mixt. of the mono- and dimethiodides, which could not be sepd. with the material at hand. The Me_2 deriv. is a much weaker base than the Me_2 deriv. A very pure sample of A gave a monomethiodide; since A does not behave as a diacid base, the above results point definitely to its being the 2,6-deriv.

C. J. WEST

Aldehyde derivatives of rhodanines and their fission products. II. LEON GENDEL-MAN. *Monatsh.* 43, 537-43(1923); cf. Andreasch, C. A. 13, 1833.—*Isopropylthiolcinnamic acid*, $Me_2CHCH_2CH:C(SH)CO_2H$, is obtained by the action of $AmONa$ upon β -cuminalrhodanine in $AmOH$ as small yellowish needles, and is transformed into the disulfide, $C_{12}H_{16}O_2S_2$, by alc. I, yellow needles, m. 190°. β -*p*-Chlorobenzal- γ -phenyl rhodanine, from phenylrhodanine and ClC_6H_4CHO , yellow needles, m. 148°. Fission with $Ba(OH)_2$ gives *p*-chlorothiolicinnamic acid, yellowish white needles, m. 157°. β -*p*-Chlorobenzal-thiohydantoin, yellow needles, sinter 230° but do not in β -*p*-Toluyldene- γ -phenylrhodanine, yellow needles, m. 136°. *p*-Methylthiolcinnamic acid, fine yellow needles, m. 159°. Disulfide, fine yellow needles, m. 212°. Methylbenzylthiocinnamic acid, $MeC_6H_4CH:C(SC_6H_5)CO_2H$, small, pale yellow needles, m. 131°. β -3,4-Di-

hydroxybenzylrhodanine, yellowish brown powder, does not m. 270° . The alk. soln. is reddish violet, the acid, yellow. Attempts to prep. a thiol deriv. failed. γ -*Camphylrhodanine* (A), thick, reddish yellow oil. The benzal compound forms bright yellow needles, m. $49-50^{\circ}$. β -*Dimethylaminobenzal compound*, orange-red needles, m. 129° . *Camphylrhodanine-2-indolindigo*, from A and isatin, dark red glistening needles. β -*m-Nitrobenzal compound* of A, pale yellow needles, m. 126° . C. J. WEST

Varying valency of platinum with respect to mercaptanic radicals. PRAFULLA C. RAY. *J. Chem. Soc.* 123, 133-41 (1923).—Tervalent Pt is represented by the compd. from thiodiazole and PtCl_4 , $\text{C}_{10}\text{H}_{15}\text{N}_3\text{S}_2\text{Pt}$ (C. A. 13, 2858), best formed from 0.5652 g. of the K salt in 10 cc. H_2O and 2 cc. H_2PtCl_6 (1 cc. = 0.0301 g. Pt). If a more dil. soln. is used, the compd. $\text{C}_{10}\text{H}_{16}\text{N}_4\text{ClS}_2\text{Pt}$ results, in which the Pt is quinquevalent. The reaction of $\text{HSC}_2\text{H}_5\text{SK}$ and PtCl_4 leads to Pt $(\text{SC}_2\text{H}_5\text{SH})_x$, where x is 3, 4, 5, 6, or 8. At lab. temps., hexavalent Pt compds. are usually obtained; but by varying the concns. of the parent solns., quinquevalent compds. have been obtained at this same temp. If the temp. be reduced to $5-15^{\circ}$, only octavalent compds. will be produced; at $60-65^{\circ}$, quinquevalent compds. result, at about 80° , quadrivalent ones and at about 100° the product is uniformly trivalent. At intermediate temps. mixts. are formed. The particular valence which Pt will assume is a function of either of the 2 variables, concn. and temp. In the case of Et_3S , the Pt compd. may be octavalent, hexavalent or quinquevalent. $(\text{C}_2\text{H}_5)_3\text{S}_2$ and PtCl_4 yield compds. in which the Pt may be considered as quadrivalent or quinquevalent. C. J. WEST

Correction on the composition of chelalbins. P. KARRER. *Helvetica Chim. Acta* 6, 232 (1923).—Chelalbins are the reaction products of alkyl Mg salts and chelerythrine (cf. C. A. 11, 2798). Recent analysis has shown that the % of N previously reported was about 1% high; in accordance with the new value the formula become $\text{C}_{20}\text{H}_{17}\text{NO}_4$; the compds. are alkyldihydrochelerythrines. N. A. LANGE

Benzopyronesulfonic acids and coumarin mercaptans. MARGARETE KRÜGER. *Ber.* 56B, 480-8 (1923).—*4,7-Dimethylcoumarin-6-sulfonic acid* may be obtained by sulfonation with H_2SO_4 contg. 20% SO_3 ; after soln. at room temp., the reaction mixt. is heated 1.5 hrs. at 80° . The acid forms small needles, m. above 285° . Sodium salt, needles; potassium salt, leaflets; ammonium salt, glistening crystals easily sol. in H_2O . The chloride may be prepd. from the dry Na salt and PCl_5 at $160-70^{\circ}$, large prisms, m. 175° . Ethyl ester, glistening needles, m. 172° . Reduced with Zn dust and HCl in EtOH , the chloride gives *4,7-dimethylcoumarin-6-thiol* (A), small needles, m. 255° . *4-Methylcoumarin-6-sulfonyl chloride*, pale yellow rhomboids, m. 137° . Ethyl ester, long, glistening needles, m. $151-2^{\circ}$. *4-Methylcoumarin-6-thiol*, yellow rhombic prisms, m. $180-1^{\circ}$. *4,6-Dimethylcoumarin-8-sulfochloride*, long needles, m. 179° . Ethyl ester, m. 182° . *4,6-Dimethylcoumarin-8-thiol*, needles, m. 246° . In prep. *3,4,7-trimethylcoumarin-6-sulfonic acid*, it was necessary to use 50% SO_3 and heat several hrs. on the H_2O bath; it is easily sol. in H_2O and m. above 300° . Sodium and lead salts, needles; potassium salt, plates. The chloride forms small thick needles and stars, m. 214° . *7-Methoxy-4-methylcoumarin-6-sulfonic acid*, isolated as the sodium salt, needles; potassium salt, yellowish green leaflets; barium salt, amorphous. The chloride forms glittering rhomboids, m. 201° . Ethyl ester, thick needles, m. 199° . *7-Methoxy-4-methylcoumarin-6-thiol*, glistening leaflets, m. 178° . All the thiols form insol. salts with Hg and Pb. They are capable of forming dibromides, that of A forming long needles, m. 271° . It is quickly decompd. by H_2O or by moist air. Chromones are much more difficult of sulfonation. *2,3-Dimethylchromone-6-sulfonic acid*, analyzed as the sodium salt, which contains 4 H_2O ; the lead salt contains 2 H_2O . The free acid becomes violet on beating and dissolves in H_2O with a violet color. An excess of alkali changes this to orange. C. J. WEST

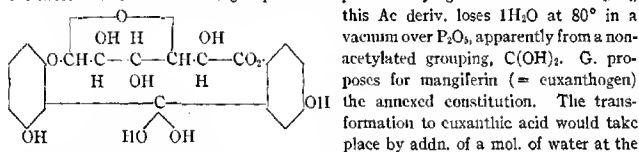
Synthesis of arylsulfone derivatives of naphtho- α -pyrones, hydroxynaphtho- α -pyrones and trihydroxybenzo- α -pyrones. JULIUS TRÖGER AND RICHARD DUNKEL. *J. prakt. Chem.* 104, 311-34 (1922); cf. *C. A.* 16, 1430.—The earlier method of synthesis was used, $1/4$ of the acid being in the form of the Na salt. 3-Benzenesulfonylnaphtho- α -pyrone, $C_{19}H_{13}SO_4$, results simply by mixing β - $C_{10}H_7CHO$ and $PhSO_2CH_2CO_2H$ in Ac_2O in the cold, pale yellow, compact prisms, m. 258° . The $PhNH_2$ soln. shows a splendid blue fluorescence and is yellow. It dissolves slowly in alkalies with an orange-red color. 3-*p*-Toluenesulfonylnaphtho- α -pyrone, pale yellow prisms, m. 275° . 3-*p*-Chlorobenzenesulfonylnaphtho- α -pyrone, small yellow prisms, m. 285° . When heated with 30% alkali, these compds. yield the aldehyde and a sulfone. With 10% alkali the reaction is much slower but the end products are the same. 2,6-(HO) $_2$ $C_{10}H_7CHO$ gives 7-acetoxy-3-benzenesulfonylnaphtho- α -pyrone, yellow leaflets, m. 246° . Sapon. with H_2SO_4 gave the corresponding 7-hydroxy derivative, thin yellow prisms, does not m. 270° . The yellow $PhOH$ soln. shows little fluorescence and the alk. soln. is reddish yellow. 7-Acetoxy-3-*p*-toluenesulfonylnaphtho- α -pyrone, thin yellow prisms, does not m. 265° . The 7-hydroxy derivative forms yellow needles, which do not m. 270° . 7-Acetoxy-3-*p*-chlorobenzenesulfonylnaphtho- α -pyrone, egg-yellow microcryst. mass, m. about 274° . 7-Hydroxy derivative, thin yellow needles. 2,7-(HO) $_2$ $C_{10}H_7CHO$ gives the 6-acetoxy-3-benzene derivative, yellow leaflets; 6-hydroxy derivative, thin yellow prisms. 6-Acetoxy-3-*p*-toluene derivative, yellow prisms. 6-Hydroxy derivative, flat, yellow leaflets. 6-Acetoxy-3-*p*-chlorobenzene derivative, egg-yellow prisms. 6-Hydroxy derivative, small, thin, egg-yellow prisms. 3-Benzenesulfonyl-7,8-diacetoxycoumarin or 3-benzenesulfonyldiacetylaphnetin, $C_{19}H_{13}SO_6$, from pyrogallolaldehyde, glistening needles, m. 183° . The solns. have a blue fluorescence. The corresponding dihydroxy derivative, $C_{18}H_{11}SO_6 \cdot H_2O$, forms pale yellow, glistening micronedles, m. 255° , sol. in alkali with a red color, but gives no color reaction with $FeCl_3$. The H_2O is lost at 105° . 3-*p*-Toluenesulfonyl-7,8-diacetoxycoumarin, $C_{20}H_{15}SO_6$, glistening needles, m. 234° . The dihydroxy derivative crysts. in yellow glistening needles, with $1H_2O$, lost at 105° with loss of color and luster; it m. 258° . 3-*p*-Chlorobenzene derivative, glistening needles, m. 233° . The corresponding dihydroxy derivative forms yellowish needles, decomp. 268° . 3-Benzenesulfonyl-6,7-diacetoxycoumarin or 3-benzenesulfonyldiacetylesculetin, $C_{19}H_{13}SO_6$, from hydroxyhydroquinolaldehyde, glistening needles, m. 252° . The corresponding dihydroxy derivative forms pale yellowish needles. Org. solvents give a yellow fluorescent, alkalies a brick-red soln. Aq. $FeCl_3$ gives no color. 3-*p*-Toluene derivative, $C_{20}H_{15}SO_6$, glistening needles, m. 228° ; dihydroxy derivative, yellowish needles, m. 278° . 3-*p*-Chlorobenzene derivative, $C_{19}H_{13}SO_6Cl$, glistening needles, m. 221° ; dihydroxy derivative, small, yellow needles. 3-Benzenesulfonyl-5,7-diacetoxycoumarin, $C_{19}H_{13}SO_6$, from phloroglucinolaldehyde, needles, m. 191° ; dihydroxy derivative (A), yellowish brown needles. Neither deriv. shows any marked fluorescence. 3-*p*-Toluene derivative, $C_{20}H_{15}SO_6$, m. 213° ; dihydroxy derivative (B), pale yellow needles, m. $258-60^\circ$ (decompn.); 3-*p*-chlorobenzene derivative, glistening needles, m. 211° ; dihydroxy derivative (C), yellowish micronedles. Diethyl derivative of A, yellowish white leaflets, m. 187° . In contrast with the HO compd. this shows a splendid blue fluorescence. Diethyl derivative of B, pale yellow prisms, m. 227° . Diethyl derivative of C, pale yellow compact needles, m. 226° . 10% alkali does not split this pyrone ring. It is decompd. to a slight extent by 20% alkali, but no sulfone could be extd. from the alk. liquor by Et_2O . C. J. W.

Centaureidin produced by the decomposition of centaurein, a glucoside from the roots of *Centaurea jacea* L. M. BRIDEL AND G. CHARAUX. *Compt. rend.* 175, 1168-70 (1922).—In a preceding paper (cf. *C. A.* 17, 794) it was shown that the hydrolysis of centaurein by H_2SO_4 yielded 33.68% glucose and 70.77% of a cryst. product to which the name centaureidin was given. This product, recrystd. from hot alc. and dried at

30°, yielded a yellow tasteless cryst. powder a little deeper in color than centaurein, contains cryst. 7.98% H₂O which it loses in a vacuum at 50° in 18 hrs., m. (anhyd.) 203°, is insol. in H₂O, sol. in MeOH, EtOH, AcOH, Et₂O, CHCl₃, PhOH, C₆H₆, PhMe, PhNO₂, and C₆H₅Br. H₂SO₄ forms a golden yellow soln. from which it is pptd. by H₂O. Alkalies dissolve it to a golden yellow soln. Its formula is C₁₉H₁₆O₆, (C 58.93, H 4.47%, mol. wt. by the f. p. method 335, MeO (Zeisel method) 21.46%). Centaureidin appears to be related to flavone.

L. W. RIGGS

The precursor of Indian-yellow. K. GORTER. *Bull. jard. bot. Buitenzorg.* [iii] 4, 260-7(1922).—Euxanthogen, the substance isolated by Wiechowsky from the leaves of *Mangifera indica* (cf. van Scherpenberg, *C. A.* 11, 41), is preferably named *mangiferin*. G. has confirmed Wiechowsky's formula, C₁₉H₁₈O₁₁, whence the substance is isomeric with euxanthic acid, to which it gives rise in the organism. The precursor is best prepd. from the bark, which is first exhausted with light petroleum and then with 60% alc., the latter giving a yield of 2.5% on evapn. The leaves yield somewhat less readily 1.7%. The substance forms thin, pale yellow needles, m. 271°, $[\alpha]_D^{25}$ 32.8°; unlike euxanthic acid, it does not at once liberate CO₂ from NaHCO₃, whence G. concludes that it contains no CO₂H group. FeCl₃ gives in alc. soln. a green color. Fehling soln. is reduced on prolonged heating, Bial's reagent gives a green color. CH₂N₂ yields a dimethyl ether, C₁₉H₁₈O₉(OMe)₂, m. 276°. Mangiferin crystals, from dil. alc. with 8H₂O, of which 1H₂O is lost on exposure to air and the rest at 110° in a vacuum. It yields an amorphous *heptaacetyl deriv.*, C₁₉H₁₁O₁₁(OAc)₇, m. about 150°. Euxanthic acid under the same conditions yields a cryst. *tetraacetyl deriv.*, C₁₉H₁₂O₁₀(OAc)₄, m. 176°, although the substance contains six H₂O groups. After previous drying in a vacuum over H₂SO₄,



this Ac deriv. loses 1H₂O at 80° in a vacuum over P₂O₅, apparently from a non-acetylated grouping, C(OH)₂. G. proposes for mangiferin (= euxanthogen) the annexed constitution. The transformation to euxanthic acid would take place by addn. of a mol. of water at the ester grouping, rotation of the ring on the left through 180°, and elimination of water

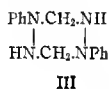
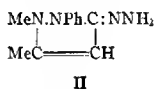
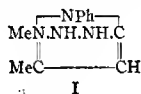
J. C. S.

The azo ester reaction of β -aminopyridine. OTTO DIELS AND GEORG BEHNEN *Ber.* 56B, 561-6(1923); cf. *C. A.* 16, 3872.— β -C₅H₄NNH₂ with (EtO₂CN)₂ gives a small yield of azodicarboxylic di- β -pyridylamide, (C₅H₄NNHCON)₂, pale yellow needles, m. 164° (decompn.). If the reaction is carried out at -20° the main product is the ethyl ester of azodicarboxylic mono- β -pyridylamide, orange-yellow, compact needles, m. 136 7° (decompn.). It decomps. vigorously under the action of dil. acids. The corresponding methyl ester forms orange-yellow needles, m. 113° (decompn.). Crystn. of the Me ester from EtOH gives the Et ester. The action of 2 mols. MeNH₂ upon the Et ester gives azodicarboxylic β -pyridylamide methylamide, dark, flesh-colored or reddish crystals, m. 137° (decompn.). With β -C₅H₄NH₂ the Et ester reacts to form ethyl- α -(2-amino-1-naphthyl)- β -(pyridylcarbonyl)carbamate, H₂NC₁₀H₇N(CO₂Et)(NHCONHC₅H₄N), glistening leaflets, m. 182° (decompn.). It forms well crystd. but easily hydrolyzed salts with HCl and HClO₄. Acetate, m. 232° (decompn.). Upon oxidation with H₂O₂ the addn. product gives the compound C₁₉H₁₇O₃N₆, dark brown needles, with bluish surface luster, decomp. 250°.

C. J. WEST

Extension and development of the Kishner-Wolf reduction method. II. ERNST THIELEPAPE AND OTTO SPRÜCKELSEN. *Ber.* 55B, 2929-39(1922); cf. *C. A.* 16, 2148.—Pyridine series.—The very slow decomn. in air of 2-hydrazinopyridine (Fargher and Furness, *C. A.* 9, 2890), accompanied by evolution of N and oxidation, is accelerated

by alkalis but the gas evolution and formation of C_3H_3N , at first very vigorous, is not complete even after 14 hrs.' boiling with KOH. On the other hand, solns. of metallic salts ($CuSO_4$, $FeCl_3$) produce a smooth evolution of N and give C_3H_3N in good yield. When citrazinic acid, $2,6,4-C_3H_2N(OH)_2CO_2H$, is hydrazinated, through the 2,6- Cl_2 acid, on the H_2O bath and N is subsequently eliminated with $CuSO_4$ the product is $2,4-C_3H_2NClCO_2H$, m. 245° , but if the hydrazination is effected with boiling $N_2H_4 \cdot H_2O$, elimination of the N yields isonicotinic acid, m. 304° . *Pyrazole series*.—The method did not give the desired result. $N_2H_4 \cdot H_2O$ heated in tubes with 1-phenyl-3-methyl-5-pyrazolone or with antipyrine splits off $PhNHNH_2$ or $PhNHNHMe$ from the ring and replaces them. The 3-methyl-5-pyrazolone primarily formed is converted, apparently under the influence of the temp. and pressure, into the bis-compd. 1-Phenyl-3-methyl-5-chloropyrazole is not attacked by $N_2H_4 \cdot H_2O$ even at 220° in sealed tubes, but its 2-methochloride ("antipyrine chloride") is hydrazinated even in the cold to *hydrazinopyrpyr*ine (I or II), a yellow oil solidifying to a glassy mass in liquid air but melting again at room temp., sol. in dil. acids and neutral to litmus; it is quite unstable but it has not been possible to decomp. it in the desired direction, *i. e.*, to replace the CO group of antipyrine by CH_3 . In attempts to effect such a decompn. there is always formed a compd., probably *1,4-diphenylhexahydro-1,2,4,5-tetrazine* (III), prisms, m. 130° , sol. in dil. acids and neutral to litmus, reduces cold Fehling soln. but is hardly attacked by boiling concd. HCl. *Picrate* of I, star-shaped crystals from alc., m. 126° . *Picrate* of III, m. 195° (decompn.). With HNO_3 III yields a *nitro compound*, $C_8H_8N_6(NO_2)_2$, yellow microcrystals from $PhNO_2$, does not m. 280° . *Monobenzoyl derivative* of III, prepd. by the Claisen method with powdered K_2CO_3 in dry Et_2O , m. 90° . *Dimethyl iodide* of III, m. 188° .



C. A. R.

Condensation of collidine with acetaldehyde. H. KONDO AND T. TAKAHASHI. *J. Pharm. Soc. Japan* No. 487, 775-80 (1922).—Using Koenigs and Benthelm's method (*Ber.* 38, 3907), K. and T. heated equiv. amts. of collidine and paraldehyde, at $210-5^\circ$ for 14 hrs. and obtained a base b_p $110-1^\circ$. Au salt, yellow, plate-like crystals, m. 135° ; Pt salt, decomp. $205-6^\circ$; Hg salt, needles, m. $192-3^\circ$. Analysis of the Au salt shows this base to be a *dimethylpropenylpyridine*, $C_{10}H_{13}N$ (A). When A was oxidized with 20 parts of HNO_3 (25%), an α',γ -dimethylpyridinecarboxylic acid was obtained which is identical with the oxidation product obtained by Alter (*Ann.* 237, 185) from *sym*-trimethylpyridine. Thus the propenyl nucleus must be in the α -position. A is therefore α',γ - $C_3H_2NMe_2CH:CHMe$. Reduction of A with Pt-H was unsatisfactory. With Na and abs. alc. was obtained γ,α' -dimethyl- α -propylpyridine (B), a strongly optically active oil, b. 184° . HCl salt of B, needles, m. $204-6^\circ$; Pt salt, orange, boat-shaped-plate needles, decomp. 210° ; both the Au and Hg salts are oily. S. T.

Free ammonium radicals. IV. Further investigations on *N,N'*-dibenzyl- γ,γ' -dipyridinium and its homologs, as well as the so-called *N,N'*-disubstituted tetrahydro- γ,γ' -dipyridyls. ERNST WEITZ AND THEODOR KÖNIG. *Ber.* 55B, 2864-89 (1922); cf. C. A. 16, 2516.—As reported in paper III, the deep blue MeOH soln. of *N,N'*-dibenzyl- γ,γ' -dipyridinium (A) reacts with NO but at the time no product of the reaction could be isolated; the resulting brown-yellow soln. again became deep blue on heating or treating with alkali or with Zn dust and acid and then showed all the sensitiveness to air of the radical A. It has now been found that on carrying out the reaction with NO in $CHCl_3$ instead of MeOH there can be isolated a cryst., almost colorless product

(B), very difficultly sol. in CHCl_3 , very easily in H_2O and alc. with alk. reaction, these solns. again showing the property of giving the blue color, sensitive to air, on heating, addn. of alkali, etc. B, however, is not a nitrosation product, but the *bicarbonate* of A with 5 mols. H_2O (a small amt. of H_2O in the CHCl_3 is essential for the reaction); the HCO_2 residues are derived from the CO_2 used to expel the air and NO, resp., at the beginning and the end of the expt.; B is obtained in much greater yield if a mixt. of NO and CO_2 is used throughout the whole expt. The blue color produced by alkalis and by Zn and acid is a general reaction of salts of A; alc. solns. become pure blue and remain clear while aq. solns. deposit a deep blue-violet ppt.; this is evidently due to a decompn. of the hydroxide of A, apparently with formation of A. The spontaneous production of a blue color on heating solns. of B is simply due to the driving off of CO_2 and decompn. of the free hydroxide resulting from the hydrolysis of the carbonate. In the formation of B, NO plays the role of an oxidizing agent, being itself reduced to N_2O . W. and K. believe that a mol. of NO adds at each of the unsatd. N atoms of A, forming an unstable "nitrosoammonium" which can easily become stabilized by a change of the "neutral part" NO into the acid radical NO, *i. e.*, by a rearrangement of the nitroso compd. $\text{R}(\text{NO})\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{N}(\text{NO})\text{R}$ into the hyponitrite $\text{RNC}_6\text{H}_4\text{C}_6\text{H}_4\text{NR} \cdot \text{O} \cdot \text{N} \cdot \text{N} \cdot \text{O}$, the A being oxidized to the hydroxide stage and the NO

reduced to the N_2O stage; in the subsequent decompn. of the hyponitrite by the CO_2 to B and N_2O there is nothing remarkable. The yield of B is about 60%. The view that NO merely acts as an oxidizer in the reaction is confirmed by the fact that B is obtained in 85% yield by the combined action of O and CO_2 on A, about 1 atom O being absorbed by 1 mol. A. O (or air) alone with A gives only very small amts. of a sol. alk. product, owing to the instability of the hydroxide. Entirely analogous to the behavior of A with NO or O and CO_2 is that of its "leuco compd.," the so-called *N,N'*-dibenzyl-tetrahydro- γ,γ' -dipyridyl (C), designated in paper III as bis-*N*-benzyl- γ -pyridinium. O and CO_2 in CHCl_3 produce only a faint (transient) blue color and there is obtained about 50% of (monomol.) *N*-benzylpyridinium bicarbonate (D), with only traces of the salt of A; NO and CO_2 produce an intense (violet-) blue color finally changing to a light dirty green; here again the chief product is D, with some of the bicarbonate of A. On reduction of salts (chloride and iodide) of A to the radical A by means of metals (without acids) in various solvents it was found that especially the blue Me_2CO solns. are characterized by their comparatively great stability towards air (they still react instantly with I); Me_2CO solns. prepd. electrolytically or directly from the cryst. A behave similarly. Furthermore, Me_2CO solns. of the dihalides can be reduced by heating with Cu wire while aq. and MeOH solns. react only with metals of greater soln. tension, such as Zn, etc., CHCl_3 as a solvent acts like Me_2CO . Designating the less resistant, more easily oxidizable state of A and consequently the more difficultly reducible halides as the ammonium- and ammonium salt-like forms and the more difficultly oxidizable state of A and the more easily reducible halides as the quinone-like forms, it appears that H_2O and MeOH favor the ammonium, Me_2CO and CHCl_3 the quinone form. However, even in the form most similar to NH_4 , A is not at all an alkali-like metal but is relatively "noble," as shown by its displacement from its salts by Zn. Since A no longer contains the original γ - or 4-H atom of the $\text{C}_6\text{H}_4\text{N}$, α - and β -alkylpyridines can yield radicals analogous to A but γ -alkylpyridines cannot. Thus, bis-*N*-benzyl-2-methylpyridinium (E), the oily, almost colorless reduction product of α -picoline-benzyl chloride gives with O the deep blue, very oxidizable radical color, as does the cryst. reduction product (F), needles from alc., m. 121° , of 2,6-lutidine-benzyl iodide. On the other hand, the oily bis-*N*-benzyl-2,4-dimethylpyridinium (G) and the cryst. bis-*N*-benzyl-2,4,6-trimethylpyridinium (bisbenzylcollidinium) (H), needles, m. $102-3^\circ$, obtained by reduction with Na-Hg of 2,4-lutidine-benzyl chloride and 2,4,6-collidine-benzyl iodide,

resp., give no trace of the blue color. With I in cold CHCl_3 all the above "leuco compds." are converted into the corresponding moniodides. On heating, e. g., in C_6H_6 , H decomps. chiefly into collidine and $(\text{PhCH}_2)_2$; apparently the monomol. radical henzycollidinium is formed by dissociation at the boiling temp. and decomps. into collidine and the PhCH_2 radical; this decompn. is shown beautifully by the results of mol. wt. detns. in boiling C_6H_6 , while in freezing C_6H_6 , the dimol. H is wholly undissociated. C behaves similarly, as shown by new mol. wt. detns.; the decrease in the apparent mol. wt. in boiling C_6H_6 and Me_2CO is not so rapid, however, as in the case of H. Probably connected with this is the following remarkable reaction: when an alc. soln. of the dichloride or diiodide of A is treated with (solid or dissolved) C or other homologous "leuco compds." (including H), the intense oxidizable blue color of the radical at once appears; W. and K. believe that all these "leuco compds." react as monomol. pyridinium radicals; themselves passing over into the moniodide, they liberate the more "noble" dipyridinium radical. Solns. of C in $(\text{CH}_3\text{Br})_2$ quickly assume the blue-violet radical color and after a short time (more rapidly on warming) deposit fine violet leaflets with a wonderful green surface luster, which are possibly a new form of the radical A, for with alc. they give the blue oxidizable radical solns. $\text{CH}_3(\text{CH}_2\text{Br})_2$ and AmBr behave just like $(\text{CH}_3\text{Br})_2$, while EtBr and PhCl give only a little of the violet crystals. H does not undergo the reaction in any of the solvents.

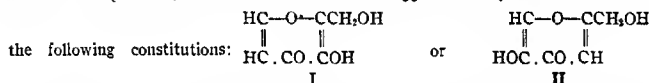
C. A. R.

Quinhydrone-like compounds of *N,N'*-dialkyl[dihydro- γ,γ' -dipyridyls]. BRUNO EMMERT AND OTTO VARENKAMP. *Ber.* 56B, 491-501(1923); cf. *C. A.* 17, 762.—Using the previously described method *tetrabenzylidipyridylviolet chloride*, $\text{C}_{44}\text{H}_{44}\text{N}_4\text{Cl}_4$ (A), was obtained as violet oblique-angled leaflets, m. 190° (decompn.). It is slightly more sol. than the corresponding I deriv.; all solns. are deep blue. The solns. in Ac_2O and AcOEt are sensitive to the air, but air may be passed through solns. in CHCl_3 , Me_2CO , PhNH_2 , and especially $\text{C}_6\text{H}_5\text{N}$ for a long time without discharging the blue color. The bromide forms dark violet oblique-angled leaflets, which behave like the chloride. The corresponding hydroxide could not be obtained pure; upon evapn. to dryness, a brownish yellow mass was obtained which no longer gave a blue soln. in EtOH . The bromide may also be obtained by the reduction of γ,γ' -dipyridyl dibromobenzylate with Zn or Mg. In the same way *tetraisoamylidipyridylviolet iodide* was obtained as deep dark violet, glistening leaflets. CrCl_3 or PhNHNH_2 is also a suitable reducing agent for prepn. of these derivs. Oxidation of A in AcOH with O of the air required 0.98 g.-atom; from the reaction product dipyridyl dichlorobenzylate was isolated as the perchlorate. If EtOH is used as the solvent, the oxidation proceeds further, due to further oxidation of the hydroxide. *sym-Dilutidyl diiodobenzylate*, $\text{C}_{44}\text{H}_{40}\text{N}_4\text{I}_2$, red prisms; *tetrabenzylidilutidylviolet iodide*, dark bronze-brown oblique-angled leaflets, m. 170° . *Dibenzyl-[tetrahydrodilutidyl]*, $\text{C}_{44}\text{H}_{42}\text{N}_4$, prepd. by the reduction of lutidine iodobenzylate with Na-Hg, pointed prisms, m. 124° . In addn. to the above mentioned reducing agents, compds. of the type of dimethyltetrahydrodicoloidyl (B) are capable of forming the quinhydrones. AgNO_3 oxidizes B, methylcollidinium perchlorate being isolated from the reaction product. γ -Phenylpyridine methiodide, nearly colorless. With Na-Hg in a H atm. this yields *N-methyl- γ -phenyldihydropyridine*, needles, m. 36° . An alc. soln. slowly reduces AgNO_3 .

C. J. WGSR

A new organic acid (kojic acid) formed by *Aspergillus oryzae*. TEIJKO YABUYA. *J. Chem. Soc. Japan* 37, 1185-1233, 1234-69(1916); cf. *C. A.* 7, 2191.—The substance is not only present in the organism, but is also formed abundantly when the latter is grown on steamed rice ("Koji") or in a 10% soln. of dextrose with salts; in the latter case, $1/10$ of the dextrose is converted according to the equation $\text{C}_6\text{H}_{12}\text{O}_6 + \text{O} = \text{C}_6\text{H}_8\text{O}_4 + 3\text{H}_2\text{O}$. The formula originally given (*C. A.* 7, 2191) must be halved, as the

result of mol. wt. detns. Kojic acid thus differs by one O atom from maltol, which is formed from carbohydrates on distn. (C. A. 4, 3223). Both substances are 3-hydroxy- γ -pyrones and give with FeCl_3 a color similar to that given by salicylic acid; kojic acid gives this reaction even at 1:200,000. The acid forms anhyd. needles, m. 152° , subliming in a high vacuum without change, readily sol. in water, alc., or EtOAc , less sol. in ether, CHCl_3 , or pyridine, scarcely at all sol. in most other solvents. The acid is pptd. by CO_2 from concd. solns. of its Na salt. It gives a red color with *p*-diazobenzene-sulfonic acid, and reduces Fehling and $\text{NH}_3\text{-AgNO}_3$ solns. The copper salt, $(\text{C}_6\text{H}_5\text{O})_2\text{Cu}$, is the most characteristic of several cryst. salts, and is employed in the isolation of the substance. The barium salt has the compn. $(\text{C}_6\text{H}_5\text{O})_2\text{Ba} \cdot 2\text{C}_6\text{H}_5\text{O}_4$; the calcium and strontium salts have a similar compn., $+ 4\text{H}_2\text{O}$. The diacetyl deriv., $\text{C}_8\text{H}_5\text{O}_2(\text{OAc})_2$, m. 102° , the dibenzoyl deriv., m. 136° , the diphenylcarbamate, $\text{C}_8\text{H}_5\text{O}_2(\text{OCONHPh})_2$, m. 170° , and the monobenzoyl deriv., $\text{C}_8\text{H}_5\text{O}_2(\text{OBz})$, m. 135° , have been prepd., the latter by BzCl in ether. The dimethyl ether, $\text{C}_8\text{H}_5\text{O}_2(\text{OMe})_2$, prepd. by CH_3N_3 or Me_2SO_4 , m. 90° , is hydrolyzed by bolliog $\text{Ba}(\text{OH})_2$ soln. into equimol. proportions of HCO_2H , $\text{MeOCH}_2\text{CO}_2\text{H}$ and $\text{MeOCH}_2\text{COMe}$. NH_3 transforms kojic acid into a base, $\text{C}_8\text{H}_5\text{O}_2\text{N}$, probably the di-Me ether of a hydroxymethylhydroxy- γ -pyridone (comenainic alc.). This base was isolated as the hydrochloride, m. $180\text{--}1^\circ$, the picrate, m. 177° , and the chloroplatinate, m. 172° . The above facts suggest that kojic acid has either of



In the case of maltol, Peratouer and Tamburello [Giorn. sci. nat. econ. 25, 272-89] decided between similar alternatives in favor of a formula analogous to I, and Peratoner and Palazzo [Giorn. sci. nat. econ. 25, 245-51] assigned to comenic acid a constitution of this type, because the latter does, and maltol does not, react with PhN_2OAc or AmNO , (only compds. of the 2nd type can tautomerically furnish the $-\text{CH}_2\text{CO}-$ grouping necessary for these condensations). Since kojic acid forms with PhN_2OAc a *benzeneazo* deriv., $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_2 \cdot \text{H}_2\text{O}$, m. (in sealed tube) $146\text{--}7^\circ$, Y. considers that it is constituted according to formula II, so that it would be 3-hydroxy-6-hydroxymethyl- γ -pyrone, the alc. corresponding with comenic acid. Various unsuccessful attempts at the conversion of kojic acid into known pyrone and pyridone compds. were made by oxidation and reduction. Br water yields monobromokojic acid, $\text{C}_8\text{H}_5\text{O}_4\text{Br}$, m. $159\text{--}60^\circ$, furnishing a copper salt, $(\text{C}_6\text{H}_5\text{O}_4\text{Br})_2\text{Cu}$, and with Ph acetate and nitrate double salts of the compns. $\text{C}_8\text{H}_5\text{O}_4\text{Br} \cdot \text{Ph} \cdot \text{OAc}$ and $\text{C}_8\text{H}_5\text{O}_4\text{Br} \cdot \text{Ph} \cdot \text{NO}_3$. It yields a diacetyl deriv., $\text{C}_8\text{H}_5\text{O}_4\text{Br} \cdot (\text{OAc})_2$, m. $94\text{--}5^\circ$, and a dibenzoyl deriv., $\text{C}_8\text{H}_5\text{O}_4\text{Br}(\text{OBz})_2$, m. $133\text{--}4^\circ$. It is converted by $\text{Ba}(\text{OH})_2$ in poor yield into hydroxykojic acid, $\text{C}_8\text{H}_5\text{O}_6$, $0.5\text{H}_2\text{O}$, which gives with FeCl_3 a transitory green or, in the presence of NaOAc , a purple color. It is probably 2,3-dihydroxy-6-hydroxymethyl- γ -pyrone and yields an amorphous copper salt, $\text{C}_8\text{H}_5\text{O}_6\text{Cu}$. When the Ph double salt of bromokojic and AcOH (above) is treated with H_2S , a sulfide, $(\text{C}_8\text{H}_5\text{O}_6)_2\text{S}$, m. $210\text{--}12^\circ$, results. (Cf. also, for maltol, Ber. 27, 806-10; 3115-20, and for isomaltol, C. A. 4, 2936; further, Brill, C. A. 10, 2940.) J. C. S.

Dissociation of *N*-pentamethylene- (or *N*-piperidyl)-*S*-triarylmethylidithiourethans with the formation of triarylmethyls. F. F. BLICKER. J. Am. Chem. Soc. 45, 544-9 (1923).—*N*-Pentamethylene-*S*-triphenylmethylidithiourethan (A), $\text{Ph}_3\text{CSCSNC}_5\text{H}_{10}$, obtained together with $\text{C}_6\text{H}_{11}\text{N} \cdot \text{HCl}$ from $\text{C}_6\text{H}_{11}\text{N} \cdot \text{HSCSNC}_6\text{H}_5$ and Ph_3CCl in C_6H_6 softens about 140° , m. $155\text{--}60^\circ$, gives Ph_3COH on attempted crystn. from AcOH or when treated with concd. HNO_3 or in Me_2CO with KMnO_4 ; with HCl it quant. yields $\text{C}_6\text{H}_{11}\text{N} \cdot \text{HCl}$ and Ph_3CCl ; on heating it evolves CS_2 ; it forms yellow solns. which readily absorb O with the formation of $(\text{Ph}_3\text{C})_2\text{O}_2$ and SO_2 . This behavior can be explained

only on the assumption that the A in soln. dissociates to some extent into the free radical $\text{Ph}_2\text{C} \cdot$. *S*-[Diphenyl- α -naphthylmethyl] analog of A, from $\text{Ph}_2(\text{C}_{10}\text{H}_7)\text{CCl}$, was not isolated; the C_{10}H_7 soln. with O gave $[\text{Ph}_2(\text{C}_{10}\text{H}_7)\text{C}]_2\text{O}_2$. The same behavior was shown by the diphenylmonobiphenylmethyl and the *p*-bromodiphenyl- α -naphthylmethyl compounds.

C. A. R.

Synthesis of α - and β -substituted quinolines. JULIUS TRÖGER AND PAUL KÖPPEN-KASTROP. *J. prakt. Chem.* **104**, 335-67 (1922).— $\text{O}_2\text{NC}_6\text{H}_4\text{CHO}$ and $\text{PhSO}_2\text{CH}_2\text{CN}$ readily condense in EtOH, with $\text{C}_2\text{H}_5\text{N}$ as the catalyst, forming α -benzenesulfonyl- α -nitrocinnamic nitrile, $\text{O}_2\text{NC}_6\text{H}_4\text{CH}:\text{C}(\text{SO}_2\text{Ph})\text{CN}$, yellowish white, fine long needles, m. 149° . Reduction with SnCl_2 and HCl in EtOH gave α -amino- β -benzenesulfonylquinoline, long needles, m. 205° , also obtained by condensing α - $\text{H}_2\text{NC}_6\text{H}_4\text{CHO}$ and $\text{PhSO}_2\text{CH}_2\text{CN}$. Hydrochloride, long, very thin needles, decomp. above 100° and decomp. by washing with H_2O . Nitrate, long needles, decomp. at 70° . Acid sulfate, yellowish white needles, decomp. above 105° and decomp. by H_2O . Acid oxalate, small needles. Perchlorate, fine needles. Chloroplatinate, reddish yellow needles contg. $1\text{H}_2\text{O}$ which is lost at 105° . Chloroaurate, golden yellow needles, m. 200° . An EtI deriv. could not be obtained. With NaNO_2 in AcOH, the base yields β -benzenesulfonylcarbostryl, long prisms, m. 312° . This was also prepd. by heating equiv. amts. of α - $\text{H}_2\text{NC}_6\text{H}_4\text{CHO}$ and $\text{PhSO}_2\text{CH}_2\text{CN}$ in a sealed tube for 2-3 hrs. at 170° , or from $\text{PhSO}_2\text{CH}_2\text{CONH}_2$ at 150 - 60° . Sodium salt, yellowish white, fine needles. Heated with the calcd. amt. of PCl_5 and a little POCl_3 at 160° , α -chloro- β -benzenesulfonylquinoline, $\text{C}_6\text{H}_4\text{NSO}_2\text{Cl}$, results, broad crystals, m. 150° . Heated 1 day with excess of EtONa, this gives β -benzenesulfonylcarbostryl ethyl ether, small prisms, m. 190° . The Cl compd. does not react with Na_2SO_4 even upon heating at 180 - 90° . Excess of PhSO_2Na , after heating several days in the H_2O bath, gives α,β -dibenzenesulfonylquinoline, $\text{C}_6\text{H}_4\text{NS}_2\text{O}_4$, fine needles, m. 204° , while an alc. KSH soln. gives β -benzenesulfonylthiocarbostryl, $\text{C}_6\text{H}_4\text{NS}_2\text{O}_4$, long, fine, yellowish needles, m. 241° , which yield methyl ether, long, yellow prismatic prisms, m. 175° , when shaken with Me_2SO in dil. alkali. α -*p*-Toluenesulfonyl- α -nitrocinnamic nitrile, long needles, m. 152° . Upon reduction this yields α -amino- β -*p*-toluenesulfonylquinoline, S-yellow prisms, m. 214° , also obtained from the aldehyde and nitrile as above. The proof of the quinoline nucleus is based upon its isolation after heating with Zn dust. Hydrochloride, long, fine needles. Nitrate, long fine needles, decomp. about 70° . Acid sulfate, long, fine needles, decomp. about 100° . Acid oxalate, long needles. Chloroplatinate, reddish yellow prisms, with $1\text{H}_2\text{O}$. Chloroaurate, fine, golden yellow needles, m. 207° . β -*p*-Toluenesulfonylcarbostryl, small, yellowish prisms from AcOH, m. 300° . This was also prepd. from the aldehyde and ester, amide and acid. Sodium salt.—Ethyl ether, cryst. powder, m. 207 - 7.5° . α -Chloro derivative, prepd. with great difficulty because of the mixt. of products usually obtained, long, fine needles, m. 178 - 9° . A product, m. 122 - 4° , is apparently the dichloro derivative. α -*p*-Chlorobenzenesulfonyl- α -nitrocinnamic nitrile, long needles, m. 156° . α -Amino- β -*p*-chlorobenzenesulfonylquinoline, yellow prisms, m. 205° . Hydrochloride, fine needles. Nitrate, thin needles. Acid sulfate, fine needles. Acid oxalate, needles. β -*p*-Chlorobenzenesulfonylcarbostryl, yellow prisms, m. 287° . Sodium salt, amorphous. Ethyl ether, fine needles, m. 173° . α -Chloro derivative, fine needles, m. 170° . β -*p*-Chlorobenzenesulfonylthiocarbostryl, yellow amorphous powder. Methyl ether, fine, long needles, m. 194° .

C. J. WEST

Preparation of α,γ -quinolines. I. S. PALKIN AND M. HARRIS. *J. Ind. Eng. Chem.* **14**, 704-5 (1922).—An improvement in the prepn. of 2,4-dimethyl-6-ethoxyquinoline based on the condensation of ethylidene-acetoac and *p*-phenetidine as described by Mikeska, Haller and Adams, *C. A.* **15**, 675. The improvements are in the treatment of the reaction mixt. after the synthesis and in the recovery of the pure substance.

G. W. STRATTON

The conversion of β -phenylhydroxylamine to quinoline bases. E. BAMBERGER AND H. WEITNAUER. *Ber.* 55B, 3376-82(1922).—Reaction between $\text{PhNH}(\text{OH})$ (A), glycerol (B), and concd. H_2SO_4 (Hindermann, *Diss. Zurich* 1897) gives quinoline (C) in extremely low yield which is increased to about 5% when acrolein (D) is substituted for B. This reaction differs from the Skraup synthesis in that the requisite O atom is taken from the A mol. instead of from, e. g., added PhNO_2 . *N*-Phenylnitrones (C. A. 14, 1971; *Ber.* 22, 720(1889)), $\text{PhN}(\text{O})\text{:CHR}$, are first formed by the condensation of A with aldehydes; on heating to higher temps. and treating with dil. H_2SO_4 they give quinolines. A mixt. of 3 g. A, 20 g. B, and 30 g. concd. H_2SO_4 was introduced slowly into a flask heated to 140° , the temp. held for 2 hrs. at 160° , the cooled mass dild. with H_2O , freed from $(\text{PhN})_2\text{O}$ by extn. with Et_2O , the H_2O layer made alk. and steam-distd.; the distillate was extd. with Et_2O , and after removal of solvent was freed from PhNH_2 by phenolation; the soln. was made alk. and steam-distd., giving 0.3 g. crude C, identified as the picrate. Substitution of KHSO_4 for H_2SO_4 gave the same result (Weitnauer, *Diss. Zurich* 1904). 30 g. D, freed from SO_2 , was added with cooling to 20 g. A in Et_2O and let stand for 2 hrs., evapn. of the Et_2O left 29.4 g. red-brown sirupy nitrone, $\text{PhN}(\text{O})\text{:CHCH:CH}_2$ (E); the best yield of C was obtained by dissolving 5.9 g. E in a little AcOH , adding 5 drops concd. H_2SO_4 , and warming on a H_2O bath; the mixt. was made alk., steam-distd., the PhNH_2 changed to PhOH , and the C distd. from the alk. soln. with steam; yield 0.21 g.; other less successful expts. are described. To a concd. very dry Et_2O soln. of 5.63 g. crotonaldehyde (*Monatsh.* 13, 516; *Ber.* 35, 1905(1902)) was added 8.85 g. A; after standing 1 day and evapn. the Et_2O , the residue was dissolved in 10 cc. AcOH , treated with 5 drops concd. H_2SO_4 , stirred 0.5 hr. on a H_2O bath, the soln. made alk. and steam, distd., the distillate extd. with Et_2O , this soln. extd. with dil. HCl , the PhNH_2 thus obtained treated with HNO_3 , etc., and the alk. soln. again steam-distd., yielding 0.8 g. crude quinaldine (F), identified as the picrate. Ciamician and Silher observed the formation of F by light-oxidation of a mixt. of PbNO_2 and EtOH , due to preliminary formation of PhNH_2 and AcH (*Atti accad. Lincei* 14, 378(1905)). [*Phenylacryl*]-*N*-phenylnitron (G), $\text{PhN}(\text{O})\text{:CHCH:CHPh}$ (Blaskopff *Diss. Zurich* 1895) sepd. freely from a reaction mixt. consisting of 3.78 g. PhCH:CHCHO and 3 g. A in 13 cc. EtOH ; it forms flat yellow needles from boiling Me_2CO , m. $155-6^\circ$. 10 g. G was dissolved in 30 cc. AcOH , treated with 10 drops concd. H_2SO_4 , let stand 2 days, warmed 10 hrs. on a H_2O bath under a reflux protected with CaCl_2 , and dild. with H_2O ; the resinous oil that sepd. was treated with excess of alkali and steam-distd.; PhNH_2 was absent, $(\text{PhN})_2$ probably present; α -phenylquinoline (H) slowly accumulated in the distillate as cryst. flocks and in soln., from which it was isolated in successive filtration and evapn. of the acidified soln., which was finally made alk. and extd. with Et_2O ; yield, 0.67 g. from 10 g. A; it was identified by its m. p. and as the picrate. A trace of H is probably formed on heating G alone at above 167° . A. R. ALBRIGHT

Echinopsine. ERNST SPÄTH AND ALFRED KOLBE. *Monatsh.* 43, 469-76(1923).—*Echinopsine* is a poisonous alkaloid found in different plants of the *Echinops* family. Gresnoff gave it the formula $\text{C}_{11}\text{H}_7\text{NO}$; it should be, however, $\text{C}_{10}\text{H}_7\text{NO}$. The behavior of this compd. upon reduction with Na and EtOH , and upon heating with PCl_5 and direct comparison proved it to be 1-methyl- β -quinoline. C. J. WEST

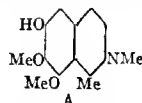
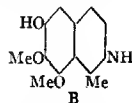
Doebner's reaction. IV. R. CRUSA. *Gazz. chim. ital.* 52, II, 43-8(1922).—In a preceding paper (C. A. 9, 1325, 1326; 10, 2888; 15, 2285) C. showed that by using $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$ in Doebner's reaction a tetrahydrogenated product and 2 reduction products of the Schiff base corresponding to the aromatic aldehyde used can be isolated besides the α -substituted β -cinchoninic acid. Having obtained the secondary products from the manuf. of α -phenyl- β -naphthocinchoninic acid (diapurin of commerce), C.

prepared tetrahydro- α -phenyl- β -naphthocinchoninic acid (A), which was purified by dissolving it in EtOH with aq. KOH and reprecip. by adding glacial AcOH: A seps. as white scales, m. 226°. The Me ester of A, m. 134°, previously described, was analyzed. The solns. of A and its salts have a slight blue fluorescence. On prolonged boiling with EtOH A gives phenyl-(β)-naphthoquinoline (B), $C_{17}H_{13}N$, m. 188°, as well as other products. The *dichromate* of B, $(C_{17}H_{13}N)_2H_2Cr_2O_7$. This reaction resembles that obtained by Simon and Maguin (*Ann. chim.* [13] 8, 361) with dihydro- α -phenyl-(β)-naphthoquinoline- β , γ -dicarboxylic acid (C). In prep. C, slightly different conditions give rise to other compds. not described. 45 g. β - $C_{17}H_{13}N$:CHPh in 55 g. EtOH were treated with 36.5 g. oxaloacetic ester and boiled 3 hrs. On cooling there sepd. a yellowish compd. (D), $C_{18}H_{15}O_4N$, m. 162° (identical with that obtained by S. and M.). From the mother liquor a yellow powder (E), m. 200°, seps. in some days. After some months another compd. (F), m. 123°, seps. Analytical results correspond to the dimer of benzal- β -naphthylamine (G), $(C_{17}H_{13}N)_2$, which with dil. H_2SO_4 gives BzH and naphthylamine quantitatively: $G + 2H_2O \rightarrow 2BzH + 2C_{10}H_7NH_2$, and of which the provisional constitution is $C_{17}H_{13}N \cdot CHPh \cdot CHPh \cdot NC_{10}H_7$. F was crystd. from EtOH

and identified as α -phenyl-(β)-naphtho- β , γ -quinolinedicarboxylic acid, yellow scales, m. 218°. In order to complete the pharmacological study of the quinolonic acids, C. prepared α -(α)-pyrrol-(H) and α -(α)-furylcinchoninic acids (I) in order to observe their influence upon the elimination of uric acid when the Ph group of atophan is substituted and to compare them with α -thionylcinchoninic acid. H gave a violet color to the urine but J showed no similar effect. 70 g. acetylpyrrole + 88 g. isatin dissolved in 70 cc. 28% KOH were heated on the H_2O -bath for 3 hrs. H was pptd. on adding AcOH; small yellow needles from glacial AcOH, blackens at 310° without melting. The sodium salt of H, $C_{11}H_7O_3N_2Na \cdot 2H_2O$, seps. as yellow needles. α -Acetylfuran (K) was obtained from Et pyromucate condensed with EtOAc and splitting the Et furylacetate obtained with 4% H_2SO_4 . 65 g. K condensed with isatin as with H gave J as yellow needles, m. 149°.

E. J. WITZEMANN

Anhalonium alkaloids. V. Synthesis of anhalonidine and pellotine. ERNST SPÄTH. *Monatsh.* 43, 477-84 (1923); cf. C. A. 16, 3303.—The fact that pellotine (A) and anhalonidine (B), when treated with MeI, yield the same compd. shows that A is to be considered as *N*-methylanhalonidine. 3,4,5- $PhCH_2O(MeO)_3C_6H_4CH_2CH_2NH_2$, treated with concd. HCl at room temp. for 1.5 hrs., splits off the $PhCH_2$ group as $PhCH_2Cl$, giving α -[3,4-dimethoxy-5-hydroxyphenyl]- β -aminoethane, isolated as the hydrochloride, amorphous mass easily sol. in H_2O , and analyzed as the chloroplatinate, light yellow ppt.; with Ac_2O and $AcONa$ this gives α -[3,4-dimethoxy-5-acetoxyphenyl]- β -acetylaminooethane, amorphous. Ring closure is brought about by heating with P_2O_5 in C_2H_5 for 20 min., giving a base which may be 1-methyl-6-acetoxy-7,8-dimethoxy-3,4-dihydroisoguinoline (C) or the 1,8,6,7-deriv., m. 105-7°. Reduction with Sn and concd. HCl gave B, m. 160°. Picrate, yellow, m. 201-8°. If C is treated with an excess of MeI in abs. EtOH for 2 days, the methiodide of A is formed, from which pure A is easily obtained in the usual way. A picrate, yellow, m. 167-9°. The probable constitutions of A and B are:



C. J. WEST

Halogen derivatives of quinine. SIGMUND FRÄNKEL, OTTO HERSCHMANN AND

CHARLOTTE TRITT. *Ber.* 56B, 433-8(1923).—In an attempt to prep. reactive derivs. of quinine (A), the Cl deriv. was 1st prepd. by the action of 4 parts PCl_5 upon 3 parts of A.HCl. Since this did not react with NH_3 , the Br deriv. was investigated. PBr_3 , however, reacted in a more complicated way. Using 3 mols. A to 7 mols. PBr_3 in CHCl_3 , the mixt. was heated 7 hrs. and then decompd. by H_2O . The aq. ext., pptd. by NH_3 , gave a carmine-red compd., apparently a *dibromide*. The H_2O -insol. portion was purified by soln. in EtOH , pptn. with dil. NH_4OH , and extn. with C_6H_6 ; finally a reddish yellow sirup was obtained which was fractionated by pptn. from AcMe by H_2O into a less sol. *tribromide*, m. 109° , $[\alpha]_D^{20} 198^\circ$, and a more sol. *tribromide*, yellowish red, decomp. $235-45^\circ$, $[\alpha]_D^{20} 198^\circ$. From 3 mols. A and 5 mols. PBr_3 , a *tribromide* m. 217° (decompn.) was obtained. If an equimol. amt. of PBr_3 is used, a *dibromide*, m. 130° , is obtained. PBr_3 gives a compd. contg. about 13% Br, while a monobromide requires 20.6% Br. Quinine chloride does not react with KBr, while with KI a brown amorphous substance was obtained which did not appear to be a mono-iodide. C. J. W.

Constitution of isochondodendrine and thebaine. FRANZ FALTIS AND THEODOR HECKZO. *Monatsh.* 43, 377-85(1923).—Since Gadamer (*C. A.* 15, 3273) found that ClCO_2Ht is a group reagent for tetrahydroisoquinoline alkaloids, its reaction was tested on isochondodendrine; the fraction crystg. from EtOH m. 180° (decompn.) and analyzed for a mixt. of $1/2$ dicarbethoxyhydrochloroisochondodendrine, $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_7\text{Cl}$, and $1/2$ dicarbethoxyisochondodendrine, $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_7$, the latter being formed by splitting off of HCl. The mixt. had $[\alpha]_D -20^\circ$ in 96% EtOH . All the Cl could be split off by heating 0.25 hr. with alc. AgNO_3 . In order to differentiate between Knorr's and F.'s formulas for thebaine, the presence of an aldehyde group in thebaizone (*C. A.* 2, 115) was tested for by Angeli and Rimini's reagent. Since the reaction was negative, F. believes that his formula has as much support as does K.'s. It will be necessary to carry out a systematic decompn. of thebaizone. C. J. WSR

γ -Chloropropylurethans and a synthesis of the 1,3-oxazine ring. A. W. DOX AND LESTER YODER. *J. Am. Chem. Soc.* 45, 723-7(1923).— γ -Chloropropyl chlorocarbonate (A), from $\text{Cl}(\text{CH}_2)_3\text{OH}$ and COCl_2 in PhMe, b_m $175-6^\circ$. Carbamate, from A and NH_4OH or from the alc. and urea nitrate nt $130-5^\circ$, b_f $135-40^\circ$, m. 62° , could not be converted into an oxazine by elimination of HCl and ring closure. Allophanate, from A and urea, m. 166° . Carbanilate, from A and PhNH_2 in Et_2O or from the alc. and PhNCO , b_f $160-70^\circ$, m. 38° , converted by refluxing in alc. with NaOH into 2-keto-3-phenyltetrahydro-1,3-oxazine, m. 96° . *o*-Methylcarbanilate, from A and $\text{MeC}_6\text{H}_4\text{NH}_2$, b_f $170-5^\circ$, m. 49° ; 2-keto-3-*o*-tolyltetrahydro-1,3-oxazine, m. 89° . C. A. R.

Molecular compounds of diketopiperazine and phenols. G. POVARIN AND P. TICHOMIROV. *J. Russ. Phys. Chem. Soc.* 52, 40-6(1920).—When 10-15% aq. solns. of diketopiperazine (1 mol.) and a phenol (1 mol.), either with or without a few drops of 10% H_2SO_4 , are boiled together for some min., cryst. mol. compds. of the 2 components are formed. These are decompd. by solvents of the phenols with the exception of water, and when heated lose phenol and do not melt, but sometimes carbonize. *Diccatechol-diketopiperazine* and *dirosorcinol-diketopiperazine*, $2\text{C}_6\text{H}_4\text{O}_2 \cdot \text{C}_4\text{H}_6\text{O}_2\text{N}_2$. *Monohydroquinol-diketopiperazine*, $\text{C}_6\text{H}_4\text{O}_2 \cdot \text{C}_4\text{H}_6\text{O}_2\text{N}_2$, forms a stable lilac form and a labile white form. *Dipyrogallol-diketopiperazine* and *protocatechuic acid-di[diketopiperazine]*. Diketopiperazine yields condensation products with protocatechualdehyde and furfuraldehyde and an unstable compd. with PhOH. The theory of oscillating affinity is applied in arriving at an explanation of the structure of these compds. J. C. S.

The reduction of an indanthrene dye by means of sodium hyposulfite. J. H. YOE AND GRAHAM EDGAR. *J. Phys. Chem.* 37, 65-73(1923).—Measurements were made of the rate of reduction and soln. of Ponsol Yellow G by alk. $\text{Na}_2\text{S}_2\text{O}_4$ solns. The dye dissolved rapidly at first, but very slowly toward the end. Soln. was most rapid in

0.5 *N* NaOH; smaller or larger concns. repressed soln. Increase in the concn. of Na ion decreased the rate of soln. From these facts it is concluded that the actual rate of reduction of the dye is rapid, and the reduced dye is slowly peptized through the agency of the OH ions to give a colloidal soln. T. S. CARSWILL.

Hydrolysis of methyl *o*-nitrobenzoate (BRANCH, MCKITTERICK) 2. Union of hydrogen with acetylene derivatives (ZALKINN) 2. Thermal analysis of the system *o*:-*p*-toluenesulfonamides (DOBRIANSKI) 2.

BOLLIGER, ADOLF: *Über Isatogene und Iso-Isatogene*. Zürich: W. Coradi-Maag. 76 pp.

CHAMBERLAIN, JOS. SCUDDER: *Textbook of Organic Chemistry*. London: Routledge. 1002 pp. 16s.

COHN, ROBERT: *Organische Chemie*. Potsdam and Leipzig: Bonness and Hachfeld. 26 pp.

ERRERA, GIORGIO: *Trattato di chimica organica*. Vol. II. Palermo: Remo Sandron. 384 pp. L 24.

HEIDELBERGER, MICHAEL: *An Advanced Laboratory Manual of Organic Chemistry*. New York: The Chemical Catalog Co., Inc. 103 pp. \$2.

MOLINARI, E.: *Trattato di chimica generale ed applicata all'Industria*. Vol. 2. *Chimica organica*. Part II. 3rd Ed. revised and enlarged. Milan: Ulrico Hoepli. 625-1406 pp. L 48. Reviewed in *Nature* 111, 142(1923).

SADTLER, S. P. and MATOS, L. J.: *Industrial Organic Chemistry*. 5th Ed. revised and enlarged. Philadelphia: J. B. Lippincott Co. 707 pp. \$8.00. Reviewed in *Am. Perfumer* 17, 555(1923).

Crotonic acid. T. OJINGA. U. S. 1,445,544, Feb. 13. Crotonaldehyde is oxidized with O while dissd. with glacial HOAc at ordinary temp. Mn(OAc)₂ and permanganate or other Mn salt sol. in the mixt. treated are used as catalyst.

Oxalic acid. G. KOLSKY. U. S. 1,446,012, Feb. 20. Sugar, starch or dextrin is oxidized with HNO₃ in the presence of H₃PO₄ at a temp. of 30-70°, oxalic acid is sepd. from the spent liquor and the latter is then denitrated and treated with fumes evolved in the oxidizing step and with air from the denitrating step to regenerate a mixt. of HNO₃ and H₃PO₄. V₂O₅ or Mo or Mn compds. may be used as catalysts.

Chlorohydrins. B. T. BROOKS. U. S. 1,446,873, Feb. 27. Material such as liquid terpene olefins contg. unsatd. substances with cyclic olefinic linking are treated in liquid form with HClO to form chlorohydrins. U. S. 1,446,874 relates to the manuf. of ethylene and propylene chlorohydrins of high concn. by adding to their aq. solns. a H₂O-sol., non-alk. salt such as NaCl, CaCl₂, Na₂SO₄, MgSO₄ or MgCl₂, sepg. the concd. portion from the more dil. portion and treating the portion which is richer in chlorohydrins with C₂H₄, CCl₄ or other solvent which is substantially insol. in H₂O.

Alkylene oxides from chlorohydrins. B. T. BROOKS. U. S. 1,446,872, Feb. 27. Alkylene oxides are prepd. from chlorohydrins, *e. g.*, oxides of C₂H₄, C₃H₆ or C₄H₈ from the corresponding chlorohydrins, by reacting on the chlorohydrin with a solid alkali, *e. g.*, NaOH or lime, while maintaining the H₂O in the reaction mixt. below 20% and distg. the alkylene oxide under reduced pressure as fast as it is formed.

Vinyl chloride. H. PLAUSON. U. S. 1,445,168, Feb. 13. Vinyl chloride is formed by reaction of HCl on nascent C₂H₂, *e. g.*, by gradually adding CaC₂ at 60-95° to concd. HCl contg. Hg ethylenedichlorosulfonate as catalyst.

Separation of aromatic from non-aromatic compounds. F. X. COVERS. U. S. 1,441,341, Jan. 9. Mixts. of satd. and unsatd. hydrocarbons with aromatic compds.

(e. g., the fraction of cracked Cal. petroleum b. 108–112°) are heated in a tube furnace (to 500–525° for the fraction mentioned) under a pressure which may reach 500 lbs. per sq. in., to alter the satd. and non-aromatic unsatd. compds. and produce derivs. of different b. p. which can be more readily sepd. by fractional distn. from the aromatic constituents, such as toluene, which remain unchanged. A mixed hydrocarbon cut from cracked petroleum may be taken at 78–82° if C_6H_4 is to be similarly recovered.

Di- and poly-halogen substitution products of monohydric phenols. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION. Ger. 349,794; cf. Chemische Werke Ichen-dorf, Ger. 281,175; Holleman, C. A. 13, 569; 15, 1705. Tri- and poly-halogen substitution products of aromatic hydrocarbons are heated at high temps. under pressure with alkali hydroxides and MeOH, or its homologs, with or without addn. of other solvents. E. g., 1,2,4,5-tetrachlorobenzene is heated with NaOH and MeOH, with or without addn. of pyridine, for about 7 hrs. at 160° under pressure, or with KOH and alc. for about ten hrs. at 200°, or with KOH and Am alc. for 16 hrs. at 200° under pressure; whereby 2,4,5-trichlorophenol is obtained; it forms lustrous needles, m. 64–5°. 2,4,5-Tribromophenol is similarly prepd. 2,5-Dichlorophenol, from 1,2,4-trichlorobenzene, NaOH, and MeOH, b. 211°, m. 58°. A mixt. of polybromonaphthols may be prepd. from mixed polybromonaphthalenes by similar means. J. C. S.

Purifying resorcinol. T. N. DISSOSWAY. U. S. 1,446,550, Feb. 27. Resorcinol is purified by extn. with cold C_6H_6 and subsequent sublimation. U. S. 1,446,551 specifies sublimation of the resorcinol and regulation of the temp. by maintaining the vapors near the exit of the heating chamber at above 115° so that vaporization of a substantial part of the resorcinol is insured, but below 135° to avoid decompn.

Alizarin or other hydroxy derivatives of anthraquinone. A. H. DAVIES. U. S. 1,446,163, Feb. 20. 2-Chloroanthraquinone is heated with an aq. soln. of NaOH and $NaClO_2$ for 24 hrs. in an autoclave provided with a stirrer, at 170°, the product is dild. with H_2O , boiled, filtered and the residue extd. with boiling dil. NaOH soln. Alizarin is pptd. by adding dil. HCl and is filtered off and washed with H_2O . A similar reaction may be effected for prepg. other compds. by substitution and addition of hydroxyls.

1-Arylamino-4-hydroxynaphthalenes. KALLE & Co., AKT.-GES. Ger. 343,057. 1,4-Dihydroxy- or 1-amino-4-hydroxynaphthalene is heated with aromatic amino compds. 1-Amino-4-hydroxynaphthalene or its hydrochloride, heated at 180° with aniline, gives 1-anilino-4-hydroxynaphthalene; this forms colorless crystals, m. 92°. When dissolved in dil. NaOH soln. and exposed to air naphthoquinoneanil [Euler, Ber. 39, 1035–40 (1906)] seps. The hydrochloride forms colorless prisms. The Me ether, $C_{10}H_{10}(OMe).NHPh$, crysts. in platelets, m. 139°. 1-o,p-Dichloroanilino-4-hydroxynaphthalene, prepd. from 1,4-dihydroxynaphthalene and 2,4-dichloro-1-aminobenzene, forms colorless needles, m. 73°. 1-p-Chloroanilino-4-hydroxynaphthalene (from p-chloroaniline) m. 96°. 1-p-Toluidino-4-hydroxynaphthalene, m. 108°, is prepd. from p-toluidine. 1-Anilino-4-hydroxynaphthalene-2-carboxylic acid (from anthranilic acid) m. 247–9°. When benzidine is heated with 1,4-dihydroxynaphthalene, it gives 4-amino-1,4'-hydroxynaphthylaminodiphenyl. The products are used in the prepn. of coloring matters. By the oxidation of their alk. solns. colored compds. of the quinone-anil type are formed. J. C. S.

Diarylguanidines. J. YOUNG AND E. G. CROAKMAN. U. S. 1,446,818, Feb. 27. An alc., ammoniacal soln. of a diarylthiourea, e. g., a soln. formed from thiocarbamide, alc., NH_3 and H_2O , is subjected to the action of Pb oxide at a temp. of about 45° in order to form the corresponding diarylguanidine, e. g., diphenylguanidine.

Aromatic amines. I. MÜLLER. U. S. 1,445,637, Feb. 20. p- $C_6H_4(NH_2)_2$ is prepd. from C_6H_5Cl by the action of NH_3 and cuprammonium sulfate as a catalyst by heating

under pressures of 250–600 lbs. per sq. in. Other amino compds. may be similarly formed.

Additive products of hexamethylenetetramine. J. D. RIEDEL, AKT.-GES. Ger. 338,427. The additive products obtained from monohalogen acetic acids and hexamethylenetetramine (Ger. 334,709) are rather unstable in soln. Their metallic salts which are more stable, are prepd. by usual methods. J. C. S.

Derivatives of hexamethylenetetramine. J. D. RIEDEL, AKT.-GES., and FR. BORDECKER. Ger. 338,428; cf. preceding pat. Hexamethylenetetramine is allowed, to react with metallic salts of monohalogen acetic acids whereby quaternary salts are formed. J. C. S.

Additive products of hexamethylenetetramine with esters of monohalogen fatty acids. J. D. RIEDEL, AKT.-GES. Ger. 346,462; cf. preceding pat. Hexamethylenetetramine is allowed to act on monobromoacetic esters of alcs. or phenols which are insol. or slightly sol. in water. The additive compd. of bornyl bromoacetate and hexamethylenetetramine is a white, cryst. powder from which borneol seps. gradually on warming with water. The additive compd. of thymyl bromoacetate (from thymol, bromoacetic acid, and phosphoryl chloride, a yellow, heavy oil, b. 153–7°) and hexamethylenetetramine forms colorless needles, m. 155–7°. Thymol is liberated on warming the aq. soln. At body temp., these compds. break up into the alc. or phenol and the antiseptic additive compd. of bromoacetic acid and hexamethylenetetramine. J. C. S.

Apparatus for subliming naphthalene, benzoic acid or phthalic acid. R. M. COLZ. U. S. 1,445,870, Feb. 20. A rotatable horizontal cylindrical vaporizing chamber is heated by a steam coil and vapors from it are led off with an air blast to a solidifying chamber.

11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

The kinetics of ester saponification by liver lipase. E. KNAFFL-LENZ. *Medd. Vetenskaps. Nobelinst.* 6, No. 3, 1–18(1922).—The study is concerned chiefly with the detn. of K , the specific reaction rate, when esters were hydrolyzed by an esterase prepn. from the press juice of beef liver. Water solns. (0.01 to 0.05 N) of Et butyrate, monobutyryn and tributyrin were used as substrates. A series of indicators was chosen that gave definite colors at definite p_H values and the ester prepn. was thereby adjusted to a definite H-ion concn. before the addition of the esterase. When the indicator showed a definite color change the contents of the flask were titrated with a standard alkali and the time was noted. Hydrolyses were carried out both in acid and alk. solns. The speed of hydrolysis of Et butyrate was directly proportional to the concn. of the enzyme and inversely proportional to that of the ester. When K is calcd. on the assumption that lipase hydrolysis is of the nature of a monomolecular reaction, its value increases as the hydrolysis proceeds if the soln. is alk. but is fairly const. if the soln. is acid. In alk. soln. K calcd. according to the formula $\pi = Kt$ gives const. results. If K is calcd. for the glycerol esters in this way it will show a progressive decrease as the action proceeds. The optimum reaction for the lipase hydrolysis of the alc. esters is p_H 7.8–8.8, while the glycerol esters are hydrolyzed better in solns. slightly more alk. A. A. C.

Specific gravity of aqueous albumin solutions. M. A. RAKUSIN AND G. D. FLIEHER. *Chem.-Zig.* 47, 66(1923).—The high viscosity of natural egg albumin (eiklar), taken in conjunction with its failure to be adsorbed by $Al(OH)_3$, led the authors to det. anew the d. of this material (com. "albumen ex ovis") in varying concn. The results ex-

pressed as d₁ for different percents of albumin are, resp.: 1.00143, 0.5; 1.00283, 1; 1.00432, 1.5; 1.00562, 2; 1.00835, 3; 1.01085, 4; 1.01341, 5; 1.01634, 6; 1.01884, 7; 1.02150, 8; 1.02410, 9; 1.02666, 10; 1.02923, 11; 1.03176, 12; 1.03432, 13; 1.03689, 14; 1.03942, 15; 1.04028, 15.35. The value 15.35% was found to be the limit of satn. for egg albumin at 17°. The above findings lead to the conclusion that natural egg albumin is a satd. soln. Since the natural product contains traces of fat, the following values were also detd. in 5% solns. of

| | du. | Angle of rotation (α). | |
|---------------------------|---------|------------------------|--------|
| albumin + fat + ash | 1.01341 | -1.83° | -38.6° |
| defatted albumin | 1.01314 | -1.83° | -38.6° |
| defatted ash-free albumin | 1.01288 | -1.83° | -38.6° |

W. O. E.

Carboligase. III. The structure of biosynthetically linked carbon chains. C. NEUBERG AND H. OHLE. *Biochem. Z.* 127, 327-39(1922); cf. C. A. 16, 108.—The *l*-phenylpyrroacemic alcohol, obtained from the action of carboligase on BzH and pyrroacemic acid, yields on decompn. with PhMgBr *d*-rotatory α -methyl- α , β -diphenylethyl-eneglycol. This on treatment with dil. H₂SO₄ goes over into α -methyl- α -phenylacetophenone, which can be identified as semicarbazone. The product of the biosynthesis by yeast is thus *l*-phenylacetylcarbinol. IV. Biosynthetic carbon chain union in fermentation processes. *Ibid* 128, 610-8(1922).—A continuation of previous studies demonstrating the biosynthetic production of *l*-phenylacetylcarbinol from benzaldehyde during the growth of yeast in starch soln. and the prepn. of biosynthetic by-products. The relation of the formation of keto alcs. on the addn. of aldehyde to fermenting yeast to phytochem. reduction is discussed.

F. S. HAMMETT

Adipocere. S. GOY AND E. WENDE. *Biochem. Z.* 131, 8-12(1922).—Of 2 samples of adipocere, the first contained crude fat 98.29, ash 0.26, CaO 0.017, MgO 0.013, and free glycerol 0.04%. The fat characteristics were: NH₃ 0.18%, refraction at 40° 32.5, sapon. no. 225.7, acid no. 194.9, Reichert-Meissl no. 13.62, Polenske no. 2.0, I no. 50.9, av. mol. wt. of total fatty acids 246.7, av. mol. wt. of H₂O-sol. fatty acids 118.6. The second sample had red and white portions which were similar on analysis. It contained crude fat 70.09%, H₂O 5.77, ash 3.37, CaO 1.34, MgO 1.05, NH₃ in fat-free portion 0.39, free fatty acids 13.31. The crude fat refracted at 40° gave 31.70, sapon. no. 231.10, acid no. 163.80, Reichert-Meissl no. 12.38, Polenske no. 1.76, I no. 57.61, av. mol. wt. of total fatty acids 230.3, av. mol. wt. of H₂O-sol. volatile fatty acids 124.7.

F. S. HAMMETT

Calorimetry. III. IV. "Thermic tonality" in the coagulation of blood and milk. T. GAYDA. *Arch. fisiol.* 19, 255-9, 261-6(1921); *Physiol. Abstracts* 6, 636; cf. C. A. 17, 1510.—Thermic tonality is not produced during the transformation of fibrinogen into fibrin, the retraction of the resulting clot, the transformation of caseinogen into casein, the pptn. of Ca caseinate, or the retraction of the latter compd.

JOSEPH S. HEPBURN

Researches on photodynamic phenomena. III. Photodynamic phenomena on the isolated heart. G. VIALÉ. *Arch. sci. biol.* 2, 231-78(1921); *Physiol. Abstracts* 7, 32(1922); cf. C. A. 16, 2872.—Under the influence of solar light, both benzoflavins and eosin modify the function of the isolated heart, acting as depressants in concd. soln. or on prolonged exposure to light, and as stimulants when the action is mild. The tonus is increased, but diminished as soon as the prepn. is placed in the dark. The action has its origin in the utilization of the energy actually absorbed by the fluorescent dye, i. e., the difference between the energy (as light) entering and that leaving the dye. Since photodynamic phenomena are usually oxidations, the benefit or harm produced by such phenomena depends on the intensity and velocity of these oxidations.

JOSEPH S. HEPBURN

Löhner's marginal eminence in the germ-free area as a support of Arndt's fundamental law. II. WALTER SEIFFERT. *Biochem. Z.* 133, 46-8(1922); cf. *C. A.* 16, 3096.—The dimensions of the marginal eminence are governed by the conditions which control the diffusion of the oligodynamic substances, and are independent of the conditions which control nutrition. Certain silver coins produce a marginal eminence on a culture of *B. coli* on Endo agar; this eminence is quite different in appearance from that due to nutrition. An intimate relationship exists between the stimulating action of minimal amts. of poisons such as oligodynamic substances, and the promotion of bacterial growth as marginal eminence.

JOSEPH S. HEPBURN

Origin of Löhner's marginal eminences. R. COBET and V. VAN DER REIS. *Biochem. Z.* 133, 49-51(1922).—Ordinary agar is superior to Endo agar as a medium for the production of marginal eminences. Their production is attributed to diffusion of the nutrient substances in the medium.

JOSEPH S. HEPBURN

Amylases of the cereal grains.—The "insoluble" amylase of barley. J. L. BAKER and H. F. E. HUTTON. *J. Chem. Soc.* 121, 1920-34(1922).—Finely ground barley was extd. first with water, then with 10% soln. of NaCl and finally with 75% alc. Portions of each of the residues were suspended in water, and either subjected to autolysis or to digestion with papain; toluene was used as a bactericide, and the period of digestion was 20 hrs. at a temp. of 30-33°. Each soln. was then filtered, and the diastatic activity of the filtrate was detd. quantitatively. By this procedure, the water-insol. amylase of barley, which is rendered sol. by the action of papain, was found to be associated with the alc.-sol. group of proteins (hordein). However, papain did not liberate amylase from isolated hordein or from barley which had been either boiled or heated to 120°; therefore papain liberated amylase from the barley residues by breaking down a preëxistent insol. enzyme complex. The amylase, which was liberated from the barley by papain, possessed the characteristic properties of the sol. amylase of barley.

J. S. H.

Superficial and internal processes. H. ZWAARDEMAKER. *Proc. Acad. Sci. Amsterdam* 24, 246-50(1922); *Verslag. Akad. Wetenschappen Amsterdam* 30, 412-7.—The chem. changes within the cell and at its surface are discussed from the viewpoint of physical chemistry and radioactivity.

J. S. H.

Probable action of lipoids in growth. D. T. MACDOUGAL. *Proc. Am. Phil. Soc.* 61, 33-52(1922).—Measurements were made of endosmosis in artificial cells provided with a plasmatic lining including lipoids; the results were correlated with measurements of the hydration reactions of biocolloids, and living and dried cell-masses in the solns. used in the osmotic tests. Lecithin had but little effect on the osmotic action when incorporated in the plasmatic jelly layer, but lessened the permeability of the system and increased the osmotic effect when deposited as a layer between the plasmatic jelly and the outer wall. When use was made of saponin or of solns. which liquify or displace lecithin in the cell contents or external layer, osmotic action was decreased, and permeability was increased presumably by increasing hydration. Saponin apparently influenced the permeability of the outer clay walls of artificial cells and of the walls of plants cells. A saponin soln. decreased the permeability of dried plates of biocolloids, which were swollen in it, but increased the permeability of plant cells. Accelerated action occurred with the artificial cell when the lipoidal layer was deposited between the plasmatic jelly and the outer clay wall. Living cell masses with a water deficit or hydration capacity of 40% absorbed approx. $\frac{1}{4}$ this amt. of water in 0.005 molar saponin soln. before shrinkage began; the effect of the saponin decreased with its concn., and attained a minimum at approx. 0.002 molar; this effect of saponin on living cell masses of *Opuntia* was not definitely accelerated by KCl. The hydration of living cell masses was not definitely influenced by changes in acidity up to pH 2; swelling was lessened in

0.01 *N* KOH, more dil. solns. yielded no definite increases. Dried (dead) cell masses were affected by saponin in approx. the same manner as living masses, but the swelling was maintained; their hydration was not definitely influenced by 0.01 *N* HCl but the swelling in concns. ranging from 0.001 to 0.0002 *N* was greater than in water; swelling also occurred in KOH soln., being noted in 0.001 *N* soln., and attaining its max. in 0.01 *N* soln. The hydration reactions of dead cell masses of *Opuntia* were those of a biocolloid contg. nearly equal amts. of proteins and pentosans. JOSEPH S. HEPBURN

Mechanism of heredity. T. H. MORGAN. *Proc. Roy. Soc. (London)* 94B, 162-97(1922).—Croonian lecture for 1922. JOSEPH S. HEPBURN

Recent advances in science—biochemistry. J. C. DRUMMOND. *Science Progress* 17, 205-8(1922); cf. *C. A.* 16, 3097.—Review of recent work on the biological value of proteins, the yeast enzymes, and S in protein. JOSEPH S. HEPBURN

Recent advances in science—medicine. A. E. HRATH. *Science Progress* 17, 236-8(1922).—Review of recent work on the relationship between sunlight and rickets and on the growth vitamins. JOSEPH S. HEPBURN

Some factors in the life history of the leucocyte. F. F. TAYLOR. *Science Progress* 17, 262-72(1922).—Review of recent work on polymorphonuclear neutrophilous leucocytes and large hyaline mononuclear leucocytes and their immunological relationships. JOSEPH S. HEPBURN

Vitalism or physical chemistry. H. GUILLEMINOT. *Scientia* 32, 226-36, 301-12 (1922).—A philosophical discussion. Irritability, and all that is associated with it, including the law of choice, have their origin in the matter and energy of the inorg. world, but have an aspect characteristic of living matter. From the viewpoint of matter, these phenomena are physicochem.; from the viewpoint of life, they are veiled in mystery. Physical chemistry professes to penetrate this veil, while vitalism worships it. The actual tendency is to lift the veil without even tarnishing its finalist colors, since the savant, in addition to a firm faith in the scientific method, also is aware of his ignorance before the unknown. JOSEPH S. HEPBURN

Equivalent mixtures in the phenomena of taste. E. VON SKRAMLIK. *Z. Sinnesphysiol.* 53, 36-78(1921); *Physiol. Abstracts* 6, 622(1922).—Solns. of various inorg. salts have tastes composed of salt, bitter, sour or sweet in various proportions. These tastes may be imitated by suitable mixts. of NaCl, quinine, tartaric acid, and glucose; the mixt. is const. for a given individual and a given salt. Most mixts. have 3 components; while 1 component may not be separately identified in the presence of the others, yet it must be present to produce the requisite complex taste; a change of 6×10^{-4} *N* in the concn. of quinine can be detected. In such expts., taste must be distinguished from tactile and olfactory sensations. JOSEPH S. HEPBURN

Denaturation of albumins during heat coagulation. W. W. LEFESCHEIN. *Kolloid Z.* 31, 342-5(1922).—Coagulation by heat consists of (1) denaturation and (2) agglutination of the albumin. Denaturation is a chem. process. The time for producing a certain turbidity was detd. by placing albumin solns. in a glass vessel $20 \times 10 \times 1$ mm. in water in a thermostat and comparing the turbidity with a ground glass. For egg albumin the temp. coeff. per 1° is 2.6; for 3% egg albumin carefully dialyzed and contg. 5% $(\text{NH}_4)_2\text{SO}_4$ it is 1.5. For 2.5% dialyzed serum albumin with 0.7% KCl the temp. coeff. is 1.6. For 1% cryst. egg albumin with 1.5% $(\text{NH}_4)_2\text{SO}_4$ it is 2.3. $T = a - b \log_e Z$, in which Z is the time of denaturation, T the temp. and a the temp. at which denaturation starts instantaneously. T is for egg albumin 66.90° , for the other albumins mentioned above 81.2° , 83.4° , 76.1° . 0.00016 *N* HNO_3 reduces the time of denaturation from 2440 sec. at 63° to 1550 sec. Formation of "acid-albumin" is disproved. Denaturation is a hydrolytic process proportional to the H-ion concn. Neutral salts increase the rate of denaturation in the order K_2SO_4 , KCl, KI, AcOK. Alkalies decrease the rate of denaturation. A. MUTSCHLELLER

Several methods of preparing ultra-visible protein sols and their significance for colloidal chemistry and biology. IV. A. FODOR. *Kolloid-Z.* 32, 103-7(1923); cf. C. A. 15, 374, 3645.—By adding thymol to egg albumin or globulin sols. large aggregates are obtained which are without Brownian movement; when weak NaOH is added so that the sols. are weakly alk. to litmus the aggregates are dispersed to primary particles in marked Brownian movement and on heating the ultramicroscopic field becomes clear. Upon adding thymol the aggregates again increase in size. Casein is prepd. by adding peptone to Ca caseinate and dialyzing upon addn. of thymol. The observations are best made in dark field illumination. The bearing of these preps. on the question of the stoichiometric or colloidal reactions of proteins is discussed.

BENJAMIN S. NEUBAUSSEN

The antagonism of albumin to globulin. G. A. BROSSA. *Kolloid-Z.* 32, 107-15 (1923).—Globulin suspensions are peptized by colloidal sols. of negative dyes (Congo red, benzopurpurin) and by positive dyes (Night Blue). Mixts. of Congo red or Night Blue with globulin are coagulated by smaller concns. of electrolytes than the dye sol by itself, this sensibility increasing with globulin content. Albumins protect both the Congo red globulin mixed sol as well as the Congo red sol. The higher the globulin content of a serum, the more sensitive it is to electrolytes when combined with Congo red. The sensitizing action of globulin may not be due to its amphoteric character for tannins act similarly.

BENJAMIN S. NEUBAUSSEN

The precipitation of serum proteins by cupric salts. SUSUMU MATSUMURA and JOHANN MATULA. *Kolloid-Z.* 32, 115-8(1923).—Serum and albumin sols. free of electrolytes are not pptd. by CuCl_2 . Pptn. takes place if the concn. of NaCl is over 0.1N, in which case pptn. increases with increase in Cu concn.; or in presence of a little alkali (soln. need not be alk. to phenolphthalein), in which case the ppt. is redissolved on further addn. of CuCl_2 . Cu salts form positive complexes with dialyzed serum proteins; combination is at other points in the mol. than those with acids. B. S. N.

The mobility of protein ions. W. PAULI. *Biochem. Z.* 127, 150-5(1922).—A const. max. valence is obtained when a protein is satd. with an excess of acid or alkali. There is also a zone in which the addition of acid or alkali causes the mean valence of the protein ion to approach more and more closely the max. valence. Under such conditions, the excess of acid or alkali present with the protein salt must be taken into consideration. Only methods which will directly det. the migration velocity of the protein ions or give the concn. of all existing kinds of ions can here be considered. By means of the potentiometer, Odén and Pauli have studied protein chlorides. The ion concns. C_H and C_{Cl} are detd. potentiometrically. $C_{Cl} - C_H$ gives the concn. of free protein ions. The total cond. K is the sum of the mobilities u, v . The mobility of the protein ions may be obtained from the formula $u_{Prot.} = \{K - (C_H u_H + C_{Cl} v_{Cl})\} / (C_{Cl} - C_H)$. A study of albumin from horse serum by this method showed that the mean protein ion mobility increased with increasing acidity to a max. with approx. 33 reciprocal ohms (R. O.) cond. at 18° and 38 R. O. at 25°. With each introduction of an acid mol. into the acid protein a linear increase in valence occurs while the ion vol. is practically unchanged by the added H ion. The ion friction is diminished by an increase in the no. of charges and the velocity is increased. The same increase in ion mobility with increasing acidity is shown for gluten and glucose. The cond. value λ_{∞} cannot easily be obtained for acid proteins because of hydrolytic dissociation at high diln. The procedure of Odén and Pauli assumes that upon max. acid satn. only a single kind of protein ion exists in the solu. and that no complex ionization of the protein salt occurs. With negative protein ions the relationships are simpler. By shaking a protein (i. e., casein, globulin, fibrin) with dil. alkali, a soln. of a protein salt of reproducible compn. is obtained. It is practically neutral and does not hydrolyze on extensive diln. Detn.

of λ and of λ_{∞} by extrapolation from the known μ enable one to calc. the mobility of the protein ion. The existence of Na_3 (caseinate)''' and of Na_4 (caseinate [case in])''' were shown by this method, the 1st. with 32.5 R. O., the 2nd. 28 R. O. at 25°. The caseinate ion has a valence of 3 as obtained by the Ostwald-Walden rule; the globulinate ion a valence of 4, and mobility of 50 R. O. Thus far no complex globulinate ions have been found. The mol. wt. of globulin is detd. as 12,000; that of casein as 3000. The methods outlined offer possibilities for the study of the mobility and other phys.-chem. properties of large org. ions of like constitution and no. of atoms, which vary only in sign of charge.

CHAS. H. RICHARDSON

Emulsin. II. RICHARD WILLSTÄTTER AND CERTRUD OPPENHEIMER. *Z. physiol. Chem.* 121, 183-94 (1922); cf. *C. A.* 17, 1251.—The hydrolysis of salicin, arbut and phenylglucoside by emulsin conforms to the monomolecular formula; the hydrolysis of helicin does not. The times required for 50% hydrolysis of helicin, salicin, phenylglucoside and methyl glucoside by emulsin stand in the relation 1 : 6 : 50 : 500. By using 8 different emulsion preps. (from sweet and bitter almonds, plums, and laboratory and commercial preps.) and comparing the periods required for 50% hydrolysis of salicin, phenylglucoside, prunasin, amygdalin, arbutin and methylglucoside with the time for the 50% hydrolysis of helicin, it was found that only in the cases of the first two was there a constant ratio regardless of the source of the emulsin prep. This would indicate that one constituent of emulsin acts upon these three compds., but that different constituents are responsible for the hydrolysis of the other glucosides. R. L. S.

A famous Frenchman. (Louis Pasteur.) ANON. *Chemist and Druggist* 97, 942 (1922).—Biography, with portrait. S. WALDBOTT

Action of radiations (DESSAUER) (BLAU, ALTENBURGER) 3.

DAKIN, H. D. *Oxidations and Reductions in the Animal Body*. 2nd Ed. Revised and enlarged. London: Longmans, Green & Co. 176 pp. 8s.

RAIMENT, P. C. and PESKETT, G. L. *Laboratory Handbook of Bio-Chemistry*. London: E. Arnold & Co. 102 pp. 5s. Reviewed in *Nature* 111, 181 (1923).

SCHMIDT, HANS. *Zur Biologie der Lipide*. Leipzig: C. Kahitzsch. 91 pp.

B—METHODS AND APPARATUS

STANLEY R. BENEDICT

An observation on phenolphthalein as an indicator. G. DE BENAVENT. *Anales soc. españ. fis. quim.* 20, 473-4 (1922).—A specimen of urine submitted for analysis was alk. and had a red color which disappeared on heating and reappeared on cooling. The patient had taken phenolphthalein as a medicament some hours previous. Expts. made by adding phenolphthalein and KOH to normal urine showed similar color changes if the urine contained uric acid. Under certain conditions solns. of benzoic and salicylic acids gave somewhat similar reactions. L. E. GILSON

Influence of the season on laboratory animals. H. ZWAARDEMAKER. *Proc. Acad. Sci. Amsterdam* 23, 1192 (1922).—In perfusion expts. with solns. contg. radioactive cations, the dose of such cations must be much smaller in summer than in winter, since the perfused organs are more sensitive in summer. JOSEPH S. HEPBURN

Calorimetry. I. Differential calorimetry. T. GAYDA. *Arch. fisiol.* 19, 1-32 (1921); *Physiol. Abstracts* 6, 440.—A detailed description is given of a differential calorimeter, and of expts. to ascertain its radiation and thermic capacity. J. S. H.

Simple quantitative determination of thiocyanate in saliva with reference to physiological and pathological conditions. A. REISSNER. *Ergeb. ges. Zahnheilk.* 6, 297-328 (1921); *Physiol. Abstracts* 6, 631-2 (1922).—The thiocyanate content of saliva is detd. colorimetrically by its reaction with FeCl_3 ; it ranges from 0.004% to 0.035% in normal individuals, and undergoes marked changes during pathological conditions. JOSEPH S. HEPBURN

New method for determination of the coagulating power of blood. M. GELERA. *Rif. med.* 37, 149-51(1921); *Physiol. Abstracts* 6, 497(1921).—The coagulability of the blood is measured by detn. of the degree of diln. with Na citrate which just prevents clotting in 1 hr. at body temp. While a relationship apparently exists between the opsonic index and the coagulability, the latter is not affected by leucocytosis. In tuberculous, even when the opsonic index is good, the clotting power is poor on account of changes in the Ca content of the blood.

JOSEPH S. HEPBURN

Estimation of hemoglobin. E. MEULENGRACHT. *Folia Haematol.*, I Abt. 27, 1-9(1921).—Observations on the working details of hemoglobin estns. by Sahli's and by Autenrieth's methods. It is held that the former is superior to the latter for clinical work.

J. C. S.

ANDERHALDEN, EMIL: *Handbuch der biologischen Arbeitsmethoden. Physik.-chem. Methoden. Untersuchung des Verhaltens gelöster Stoffe. Methoden zur Darstellung und Untersuchung flüssiger Kristalle*, OTTO LEHMANN. 123-352 pp. *Methoden z. Studium d. Funktionen d. einz. Organe d. tier. Organismus. Methoden der Muskel- u. Nervenphysiol. Untersuchungen an Muskeln u. Nerven. Methoden d. Untersuchung der elastischen Eigenschaften des Muskels mit Einschluss d. Myographie*, RUDOLF DITTLER. *Methoden d. mechan., therm., chem. u. osmot. Reizung von Muskeln u. Nerven*, PAUL JENSEN. *Thermodynamik d. bioelektrischen Ströme*, ARMIN V. TSCHERMAK. *Untersuchung d. Zuckungswärme mit thermoelek. Methoden (sogenannte myothermische Untersuchung)*, VIKTOR FRHR. V. WEIZSÄCKER. *Ergographie u. Ergometrie*, OTTO ZOTH. P. 244. *Methoden d. experimentellen morphol. Forschg. Mikroskopie u. Makroskopie. Mikroskopie einzelner Gewebe (Blut u. blutbildende Organe, usw.)*, G. HERCHBIMER. *Makroskopische Untersuchung des Zentralnervensystems*, H. OBERSTHNER. *Die Mikroskopie des zentralen u. peripheren Nervensystems*, OTTO MARBURG. *Die Methode d. direkten Beobachtung d. lokalen Kreislaufstörungen u. d. Verwertung pathologisch-anatom. Befunde i. d. Kreislauforganen f. d. Pathologie derselben*, GUSTAV RICKER. *Methoden zur morpholog. Untersuchung d. Lunge*, H. LOESCHKE. *Methoden zur morpholog. Untersuchung d. Milz*, ALEXANDER SCHMINCKE. 337-634 pp. *Physikalisch-chemische Methoden. Kolloidforschung. Methoden d. Herstellung kolloider Lösungen. Das Arbeiten mit Schutzkolloiden*, ALFRED LOTTERMOSER. *Die Methodik d. Quellungserscheinungen*, JOHANN MATULA. *Methoden zur Bestimmung d. Teilchengrösse*, H. HANDOVSKY. *Ultrafiltration*, HEINRICH BECHOLD. *Zentrifugieren u. Dialyse*, HERMANN THOMS. 131-384 pp. *Angewandte chem. u. physikal. Methoden. Pharmakologie, Pharmazie, Toxikologie. Nachweise u. Bestimmung der Gifte auf pharmakologischem Wege*, H. FÖRNER. 421-612 pp. *Angewandte chem. u. physikal. Methoden. Nahrungs- u. Genussmittel. Nahrungs- u. Genussmittel-Untersuchungen. Mikroskop. Untersuchung von Getreide, Hülsenfrüchten, Mülleerzeugnissen, Back- und Teigwaren*, C. GRIBBEL. *Die chem. Untersuchung von Getreide, Gerste, Malz, Hülsenfrüchten, Mehl, Kindermehl, Stärkemehlen, präpar. Mehley Paniermehl, Brot, Backwaren, Teigwaren, Hefe u. Backpulver*, E. SPAETH. *Gemüse u. Fruchtdauerwaren. Fruchtsäfte, Fruchtsirupe, Limonaden u. alkoholfreie Getränke—Marmelade u. marmeladenart.—Zubereitungen*, P. BUTTENBERG. *Mikroskop. Untersuchung von Gewürzen*, C. GRIBBEL. *Chem. Untersuchung von Gewürzen*, E. SPAETH. P. 516. Berlin and Vienna: Urban & Schwarzenberg.

FINZEL, OTTO. *Praktische Harndiagnostik*. 2nd Ed. Leipzig: Kruger & Co. 40 pp.

C—BACTERIOLOGY

A. K. BALLS

The influence of the culture medium on the agglutinability of the typhoid bacillus. JOS. HORN. *Münch. med. Wochschr.* 69, 7-10(1922).—Grown on clear agar, typhoid bacilli

may quickly lose their agglutinability; this does not take place so readily on agar which has not been cleared. Addition of starch, lactose, sucrose, and glycerol to the cleared agar has little or no effect in restoring the agglutinability. Mannitol, maltose, dextrose and galactose, and particularly the latter, restore or increase the agglutinability best. The addition of 1% sugar proved most advantageous. All of various strains were influenced favorably by galactose, mannitol and maltose. All other sugars influence the agglutinability of various strains differently.

S. AMBERG

Iron bacteria and their relation to algae. N. CHOLODNYJ. *Ber. botan. Ges.* 40, 326-46(1922); illus.—Small lumps of a jelly-like substance incrusting with $\text{Fe}(\text{OH})_3$ and found on the filaments of algae, particularly on *Conferia*, are described. These lumps are produced by a species of bacteria, viz., *Sideromonas conservarum*. The possibility of symbiosis between the algae and the bacteria is discussed.

F. C. COOK

Aims and methods of chemotherapeutic antiseptics. J. MORGENROTH. *Klin. Wochschr.* 1, 353-8(1922).—A virulent culture of staphylococci or streptococci (0.10 to 0.20 cc.) was subcutaneously injected into the abdomen of mice. As a prophylactic measure 1 cc. of a soln. of vucine or Rivanol (2-ethoxy-6,9-diaminoacridine hydrochloride) was injected around the infected area immediately after the introduction of the organisms. The introduction of 1 cc. of a 1:40,000 soln. of Rivanol produced complete sterility in 24 hours. A Rivanol concn. of 1:80,000 was without effect. Vucine (1.0 cc. of a 1:16,000 soln. also produced complete sterility in 24 hrs. Freshly isolated streptococci (human) are more easily destroyed by the antiseptics than old stock cultures. (Antiseptics that give good results *in vitro* may be worthless *in vivo* by M.'s method.) A Rivanol concn. of 1:16,000 produced complete sterilization in 4 hrs. The injection of 1 cc. of a 1:80,000 soln. of Rivanol gave rise to a complete sterility in 3 days. Three cc. of a 1-4,000 Rivanol soln. injected around and into the infected area 5 and 18 hrs. after the time of infection and twice repeated at 24-hr. intervals produced sterility in the infected area, as well as in the peritoneal cavity and the blood. The inflammation had disappeared completely 2 days after the last injection.

MILTON HANKE

Effect of vitamin extracts in revivifying old cultures. JEAN BROADBURST. *Abstracts Bact.* 5, 3(1921).—Approx. 20 species of bacteria, on agar cultures from 3 to 24 weeks old, were revived by a sterile water-sol. B ext. of the navy bean.

J. S. H.

The hydrogen ion concentration and the metabolism of *B. typhosus*. CORNELIA M. DOWNS. *Abstracts Bact.* 5, 5-6(1921).—The organism was grown on meat infusion broth contg. 1% dextrose and adjusted to p_H 7.4; 24 hrs. after inoculation the p_H ranged from 4.9 to 5.1; then the reaction returned toward the alk. side. Usually approx. 30% of the dextrose was used in 24 hrs.; strains giving a more acid reaction used less dextrose than those producing a more alk. reaction. When growth ceased, from 63% to 70% of the dextrose remained in the medium.

JOSEPH S. HEPBURN

Abundant but little known group of soil bacteria. H. J. CONN. *Abstracts Bact.* 5, 8-9(1921).—This group of bacteria is closely related to the alkali-forming bacteria of milk. Its members grow readily on the surface of ordinary agar, but fail to grow to any extent in liquid media.

JOSEPH S. HEPBURN

Variations in the morphology of the diphtheria bacillus due to age. HENRY ALBERT. *Abstracts Bact.* 5, 14-5(1921).—A study of the occurrence of granules in diphtheria bacteria at various stages of their development; 125 pure cultures were used, and toluidine blue-iodine was employed as a granule stain.

JOSEPH S. HEPBURN

Classification of diphtheria bacilli based on the toluidine blue-iodine method of staining. HENRY ALBERT. *Abstracts Bact.* 5, 25(1921).—This method of staining is of considerable value in distinguishing between virulent and non-virulent forms of diphtheria bacilli, since no culture capable of producing disease was found which did not contain granular types of the microorganism.

JOSEPH S. HEPBURN

Bacterial bioluminescence. III. Action of the rays from radium bromide. G. ZIRPOLO. *Boll. soc. naturalisti Napoli* 33, 75-81(1920); *Physiol. Abstracts* 7, 70(1922).— $RaBr_2$ increases the power of luminescence of luminescent bacteria. When a tube contg. $RaBr_2$ is placed in a culture of such bacteria, a layer of strongly luminescent organisms forms about the tube; this layer is surrounded by a dark ring, which is itself surrounded by a slightly luminescent zone.

JOSEPH S. HEPBURN

Some fungi from the air of sugar mills and their economic importance to the sugar industry (VAN DER BIJL) 28.

BERGEY, DAVID H., et al. *Manual on Determinative Bacteriology*. Baltimore: Williams & Wilkins Co. Prior to publication (April or May) \$3.50, U. S., Canada, Mexico, Cuba; other countries, \$3.75. After publication, \$4.50, U. S., Can., Mex., Cuba; other countries, \$4.75.

BRUYNOGHE, R.: *Handbook der Bakteriologie*. Amsterdam: Feikema, Caarelsen & Co. 355 pp. Fr. 25.

CONN, H. W. and CONN, HAROLD J.: *Bacteriology*. Baltimore, Md.: Williams & Wilkins Co. 441 pp. \$4, U. S., Canada, Mexico, Cuba; other countries, \$4.50.

WALBUM, L. E.: *Studier over Dannelsen af de bakterielle Toximer*. Kopenhagen: Levin and Munksgaard. 193 pp. Kr. 10.

D—BOTANY

B. M. DUGGAR

Composition of domestic plants in successive periods of growth. J. G. MASCHHAUPT. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* 27, 125-32(1922); cf. C. A. 15, 3132.—Samples are taken weekly—from May to August—from wheat which was sown in March. An analysis of the compn. of the ash shows that the ripe wheat contains more N, P_2O_5 , SiO_2 , Na_2O , MgO , and Fe_2O_3 than the unripe, however, less SO_2 , Cl, K_2O and CaO .

R. BRUTNER

A criticism of beutner's theory of the electromotive force of diphasic liquid systems and their relation to bio-electrical phenomena. DOROTHY HAYNES. *Ann. Botany* 37, 95-103(1923).—B. made expts. on 2-phase systems, water and oil, and from their properties concluded that it is the salt rather than the acidity of the cell which detes. its elec. behavior. B.'s expts. are discussed.

F. C. COOK

Experiments on the growth of fungi on culture media. W. BROWN. *Ann. Botany* 37, 105-29(1923).—A continuation of C. A. 16, 4251. Expts. on the growth of *Sphaeropsis malorum* and *Fusarium* sp. on potato agar were studied in detail. The relative amt. of staling (falling off of growth from the max.) can be modified by varying the depth of the medium and particularly by providing for disposing of CO_2 and NH_3 , 2 volatile products of metabolism. The amts. of NH_3 formed in *Sphaeropsis* cultures on a no. of media were detd.

F. C. COOK

Forcing the germination of freshly harvested wheat and other cereals. G. T. HARRINGTON. *J. Agr. Research* 23, 79-100(1923).—The embryos are never dormant, dormancy being imposed by coat structures. Relations of O_2 appear to be very important in the germination of freshly harvested cereals. The beneficial effects of mechanical treatments, artificial drying and heating are probably related to increased O_2 supply to the embryo. It seems likely that the permeability of coat structures to O_2 increases during after-ripening and that this condition is related to the improved germination.

F. C. COOK

Polymerization of formaldehyde by plants in the dark. T. SABALITSCHKA. *Ber. pharm. Ges.* 32, 278-301(1922).—Preliminary expts. with HCO_2H and certain plants like *Elodea canadensis* in the light show some conversion of the acid to starch. Other expts. with CH_2O and the same plant (also *Tropaeolum majus*) in the dark indicate

fixation and conversion of the aldehyde, probably to sugar and starch, and indeed in the chlorophyll tissues, thus strengthening Baeyer's assimilation hypothesis. W. O. L.

A reaction of wood with remarks on anethole. O. ADLER. *Biochem. Z.* 128, 32-4(1922).—When bits of wood are placed in a concd. soln. of phenylhydrazine-HCl in AcOH and warmed they become colored an intense green. The coloration also occurs after long standing at room temp. Adhering bark becomes red or red-brown. These changes occur with many species of wood. Furfural and old preps. of anisole and fenchol give the same reaction. Furfural is not considered the substance which gives the reaction in wood because it does not occur in detectable amts. under these conditions and because the pentosans of the wood do not give the green coloration. Pure anethole does not yield the test, after concn. on the water bath; or when fuming HNO_3 is carefully added by drops; or when oxidized by KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, and H_2SO_4 ; or when treated with ultra-violet light for several hrs.; still the green coloration takes place under the conditions described. Ozone or strong sunlight produces a similar result. The known oxidation products of anethole, anisaldehyde and anisic acid do not undergo coloration in the test, nor do anisole, anisoin, isoanethole and metanethole, safrol, eugenol, isoeugenol, cinnamaldehyde or coniferin. It is probable that some other deriv. of anethole is the basis of the described reaction. F. S. HAMMETT

Recent advances in acience—plant physiology. WALTER STILES. *Science Progress* 17, 216-21(1922).—A discussion of the chem. factors concerned in the formation of flower and fruit. JOSEPH S. HEPBURN

Recent advances in science. Plant physiology. CYRIL WEST. *Science Progress* 17, 371-6(1923).—Review of recent work on after-ripening, dormancy, and methods of terminating the dormant periods of seeds. JOSEPH S. HEPBURN

Effect of different kinds of solar radiation on the formation of essential oils in plants. E. CANALS. *Bull. Sci. Ind. Roure-Bertrand fils* (iv) 3, 8-13(1921).—Plants of *Thymus vulgaris* were grown under glass of different colors. Plants receiving white and blue light were little different from open-air plants. With red light, however, growth was altered and flowering inhibited. The essential oil from plants under red light contained 25.5% of thymol, from plants under blue light, 36% of thymol, and under white light, 45% of thymol. The oil from open-air plants contained 52.5% of thymol. The thymol content of the oil decreases with the decrease in the xerophilous character of the plants. J. C. S.

The infestation of fungus cultures by mites. (Its nature and control together with some remarks on the toxic properties of pyridine.) S. T. JEWSON AND F. TATTSFIELD. *Ann. Appl. Biol.* 9, 213-40(1922).—*Aleurobius farinæ*, *Tyroglyphus longior* and *Glyciphagus cadaverum* are serious pests of fungus cultures. Pyridine b. 114-7°, and concn. pyridine h. 94-140° are equally efficient in controlling them. Pyridine has a slight toxicity to fungi; this is not objectionable in practice especially if the cultures are subcultured. NH_4OH and its vapor are more toxic than pyridine, but are also considerably more toxic to the fungi. NH_3 vapor, however, is useful to rid lab. app. of mites. Minute doses of pyridine have a powerful paralyzing effect on mites. Up to about 0.25% concn., it has very little toxicity to *Aspergillus niger*; above this concn., toxicity increases rapidly. There were no indications that pyridine possessed food value for the fungus. Its toxicity to fungi lies chiefly in its basic properties which are not due to the modification of the pH value of the medium. Mol. for mol., aniline was more toxic to mites than pyridine, but the low vapor pressure of the latter limited its toxicity. CHAS. H. RICHARDSON

Variations and migrations of saccharine matters in *Mercurialis perennis* in the course of its annual vegetation. P. GILLOT. *J. pharm. chim.* 26, 250-8(1922).—The results of detg. at different seasons of 1 year the optical rotations of exts. before and after inversion are given in 6 tables. The proportion of initial reducing sugar varies but little

in the aerial parts of the plant, at least while it is in full assimilating activity. In the underground organs of growth (shoots), the amt. of reducing sugar is always high regardless of season. In old organs, rhizomes, and roots, it reaches a max. in summer when the leaves are active in elaborating the reserves, and diminishes while the plant grows underground. It is at a min. in spring soil when the shoots come out of the ground. As to the *polysaccharides* elaborated by the plant, the aerial parts, also the shoots while underground (between Aug.-Sept. and spring) yield exts. whose optical changes under the action of invertase clearly indicate *sucrose*. But after fruiting the reserve organs of the plant, i. e., rhizomes, roots, and subterranean shoots, furnish exts. which clearly differ from the former by the persistence of the + rotation after hydrolysis. This suggests the presence in these organs of a *dextro-rotating principle different from sucrose*. The proportions of this compd. vary with vegetative seasons. Low in the flowering season, it suddenly increases as soon as the leaves have reached their complete development, and it persists in notable amt. up to the "August sap"; then it seems to decrease. G. obtained much sucrose from rhizomes collected in December; the other sugar referred to has not yet been isolated.

S. WALDBOTT

The actual sugar content of the rhizome of reeds and reed mace. TH. SABALITSCHKA. *Chem.-Zig.* 47, 80-1(1923).—Recent statements of sugar content and possible alc. production have been greatly exaggerated. The roots contain never more than 5% of cane sugar and generally much less.

E. D. WILLIAMSON

Variations in the Concord grape during ripening (NOYES, *et al.*) 12. Beneficial results from the inoculation of canning peas with legume bacteria (WRIGHT) 15. Atmospheric pollution by industrial wastes (SWAIN) 13. Precursor of Indian yellow (GORTER) 10. Carob-tree manna and its sugar (CHARAUX) 10.

E—NUTRITION

PHILIP B. HAWK

NORMAL

The influence of cod-liver oil on the calcium metabolism. B. SJOLLEMA. *Arch. néerland. physiol.* 7, 384-91(1922).—The administering of cod-liver oil to rabbits causes a keeping back of Ca in the organism no matter whether the food of the animal is rich or poor in Ca. The food of the animals used for these expts. is otherwise free from fat, contg. only carbohydrates, casein, some salts, and vitamins. Cod-liver oil causes a diminishing of the secretion of Ca by the kidneys as well as by the intestinal tract; the secretion by the kidneys takes place essentially if the diet is poor in Ca. With a diet rich in Ca the quantity of the feces as well as their Ca content decreases if cod-liver oil is given. The expts. prove that the organism can give off larger quantities of Ca than are taken up. The secretion of the phosphoric acid runs nearly parallel with the secretion of Ca.

R. BEUTNER

Calcium metabolism. R. ROSEBMAN. *Arch. néerland. physiol.* 7, 358-61(1922).—Metabolism expts. in man are described which prove that 0.715 or in another expt. 1.43 g. CaO, taken per day in the form of a CaCl₂ soln., are entirely resorbed. The Cl is secreted by the kidneys. The expts. further prove that abundant eating of meat leads to a loss of CaO in the body. This loss of CaO is likely to be one of the conditions leading to hay-fever; CaCl₂ is, therefore, successfully used as a remedy. The retention of Ca also leads to a retention of K. The taking up of Ca salts not only changes the Ca content of the body but thoroughly displaces the ionic equil.

R. BEUTNER

Basal metabolism. DAUTREBANDE AND WHITRIDGE DAVIES. *Bull. acad. roy. med. Belg.* [5] 2, 147-79(1922).—A description is given of the well known method of indirect calorimetric detn. of the basal metabolism by measuring the consumption of O during a definite time. Every l. of O₂ corresponds to 4.572 cal. (as a middle value) with

respiratory quotient of 0.76. The best method of measuring the consumption of O_2 is the collection and subsequent analysis of the expired air as the authors describe it. This method is simplified by collecting the expired air in a Douglas sack. The app. used consists of the Haldane mask, a flexible tube, the sack for collecting the air and valves as well as a gas meter for measuring the quantity of the expired air. The authors devote an extensive study to the influence of various methods of observation. The application of pure O_2 does not seem advisable as it irritates certain nerve centers, and, therefore, produces changes in the respiration. Another physiol. abnormality may be produced in the respiratory organs by the resistance of the mask. Various types of masks are studied for that end. The result is that the Haldane mask is the only one which does not produce any change in the normal respiration. To avoid errors, due to absorption of the expired CO_2 in the collecting sack, the analysis of the expired gas should be made immediately after collecting. The application of the method to clinical cases exhibiting a metabolism lower or higher than normal is described.

R. BRUNNER

Common defects of diet and their pathological significance. E. MELLANBY. *Brit. Med. J.* 1922, 1, 790-1, 831-3.—A resumé, dealing chiefly with vitamin deficiencies.

A. T. CAMERON

Variations of the respiratory quotient of the vitamin-deficient pigeon. Influence of intravenous injections of glucose. H. MAGNE AND S. SIMONNET. *Bull. soc. chim. biol.* 4, 419-25(1922).—Pigeons whose diet is deficient in vitamin B show a lowering of respiratory quotient characteristic of starved animals or those on a non-carbohydrate diet. Digestion is markedly affected, and the defect in absorption can in part explain the low respiratory quotient. Parenteral administration of glucose shows that there is also defective tissue oxidation.

A. T. CAMERON

Value of colostrum to the newborn. GLADYS L. BOYD. *Can. Med. Assoc. J.* 12, 724-5(1922).—Blood of 10 newborn infants before ingestion of any food contained relatively small quantities of globulin and negligible amts. of euglobulin. In 7 infants receiving colostrum within a few hours after birth there was a marked and early rise in the euglobulin and pseudoglobulin, and an increase in the proportion of total globulin. In 3 infants deprived of colostrum the globulin content of serum remained low and euglobulin was present only in traces.

A. T. CAMERON

Ultra-violet absorption spectra of extracts containing vitamins. HORACIO DAMIANOVICH. *Anales asoc. quim. Argentina* 10, 209-14(1922).—Illustrated with many spectrographs. Vitamin B. Solns. of ext. of brewers' yeast, although practically colorless, showed a characteristic absorption band between 2478 and 2660 Å. which seems to correspond to the pyrimidic compds. which serve as absorbents of nucleic acid. Vitamin A. A 4% soln. of oil from yellow maize in a mixt. of EtOH and Et₂O showed a characteristic absorption band in the extreme violet region between 4900 and 4000 Å. and another band in the ultra-violet between 8500 and 2800 Å. Olive oil and oil from white maize showed no such bands and it is known that these contain no vitamin A while oil from yellow maize does. A soln. of the pigment from yellow maize gave an absorption band in the violet similar to the oil but no band in the ultra-violet.

L. E. G.

Vitamin-B method for separation. S. TSUKIYE. *Biochem. Z.* 131, 124-39(1922).—Rice-bran exts. contain before hydrolysis choline, glucose and levulose; the purine bases, adenine and hypoxanthine; the amino acids, arginine, lysine, etc., but no histidine nor tryptophan. Vitamin B is not pptd. by Pb acetate from acid solns. It is completely pptd. by phosphotungstic acid from H_2SO_4 or HCl solns.; by $AgNO_3$ in the presence of BaO in neutral or weakly alk. solns.; by ammoniacal $AgNO_3$ solns. but is sol. in excess NH_4OH ; by picric and tannic acids, the former being sol. in alc. and hot H_2O . A part is pptd. by $HgCl_2$ but not by Au or Pt chlorides nor picronic acid. The biuret, Schmidt's, Millon's, Weidel's, xanthine, murexide and diazo reactions are all negative. The

Folin-McCollum-Denis uric acid test is weakly positive. This latter is apparently not due to vitamin B itself. Vitamin B in neutral condition is not sol. in alc. more concd. than 80%, but is easily sol. in acid alc. and H_2O . It is both anti-neuritic and growth-promoting. It is markedly absorbable by animal charcoal and metallic sulfides particularly. It is also dialyzable. T. prepd. it by extg. 1 kg. of rice-bran with 3 l. H_2O for 2 hrs. on the water-bath and filtering. The filtrate was evapd. on the water-bath to a thick sirup, 75% alc. was added and the ppt. removed. The alc.-sol. fat and lipoids were removed with Et_2O . The residue was dissolved in H_2O and pptd. by Pb acetate with care not to use an excess. The ppt. was removed and the Pb removed as sulfate with dil. H_2SO_4 . The filtrate was pptd. by concd. phosphotungstic acid in 5% H_2SO_4 , and the ppt. washed with 5% H_2SO_4 , decompd. with BaO, the BaO removed from the filtrate, which was acidified with HNO_3 and treated with $AgNO_3$. The ppt. was filtered off and the filtrate made weakly alk. with $Ba(OH)_2$ soln. The resultant ppt. was dissolved in dil. H_2SO_4 and freed from Ag with H_2S . The H_2SO_4 was removed, the neutral soln. acidified with HNO_3 and evapd. to dryness. The residue was extd. with 10% $AgNO_3$ soln. and ammoniacal $AgNO_3$ added to the filtrate. The ppt. was dissolved in dil. H_2SO_4 and the Ag pptd. out with H_2S . The filtrate was concd. and to it was added 10 times its vol. of abs. alc. The ppt. was sepd. by centrifugation, washed with abs. alc. then with Et_2O and dried in a desiccator. It is gray-white powder; it cures avian polyneuritis in doses of from 5 to 6 mg. From 4 kg. bran 0.3–0.5 kg. of product are obtained.

F. S. HAMMETT

Studies on metabolism at both high and low altitudes. II. Elimination of carbon dioxide by the kidney. A. COSTANTINO. *Arch. sci. biol.* 2, 147–60(1921); *Physiol. Abstracts* 6, 517(1921).—Guinea pigs were kept at reduced atm. pressure. The elimination of CO_2 by the kidneys increased from a minimum during the first 24 hrs. to a max. at the end of the third or fourth day; a decreased excretion of P_2O_5 and an increased respiratory rate also occurred. Then the amt. of CO_2 excreted, and the concn. of the OH ion gradually decreased while P_2O_5 and NH_3 increased, the latter attaining values greater than in normal urine.

JOSEPH S. HEPBURN

A Berlin review of bios. M. IRE. *Compt. rend. soc. belge biol.* 1921, 253–4; *Physiol. Abstracts* 6, 376(1921).—Bios is at least inseparable from, if not identical with, the antiberiberi vitamin.

JOSEPH S. HEPBURN

Food accessory factor in relation to the teeth. P. R. HOWE. *J. Dental Research* 7–12(1921).—When guinea pigs were fed a diet rich in starch and sugar for a period of 6 to 12 months, the oral flora became acid-forming in character, but no effect could be found upon the teeth, even when microorganisms (such as *B. acidophilus*) were isolated from carious teeth and added to the ration for several mouths. When teeth were kept for 6 months in saliva mixed with dextrose, maltose, lactose, sucrose, dextrin, white flour, and bread, some were unchanged, some etched, and some decalcified; the general effect was that of a weak decalcifying agent. When exptl. animals, chiefly guinea pigs, were fed on a diet deficient in vitamins and consisting almost entirely of fat-free milk and rolled oats, decalcified areas were produced in the teeth, the alveolar process, the bones of the skull, and even in other bones of the body. Recalcification was produced by return to an adequate diet. Symptoms of pyorrhea alveolaris and of dental caries were noted.

JOSEPH S. HEPBURN

Nutrition, growth and dentition. MILO HELLMAN. *Dental Cosmos* 65, 34–40 (1923).—A study of the influence of nutrition on growth and dentition. Acceleration in body growth has an adverse influence upon the process of dentition. J. S. H.

Report on the food requirements of man and their variations according to age, sex, size, and occupation. Food (War) Committee, Royal Society, 19 pp.(1922).—On account of refuse and waste, food as purchased should have a utilizable caloric value

approx. 10% higher than the cal. actually required by the individual. The basal metabolism of an av. man (body wt. 66 kg., height 171 cm., age 25 to 50 yrs.) is 70.3 large cal. per hr.; approx. 300 cal. are required daily for purposes of locomotion. The total energy requirement of a man in 24 hrs. is the sum of: (1) basal metabolism during 8 hrs. sleep, (2) basal metabolism increased by 30% during 8 hrs. free time, and (3) basal metabolism plus the work increment (mech. work performed, measured in cal., multiplied by a factor varying between 3 and 8, usually 5) for 8 hrs. The total caloric requirement of an av. American man (body wt. 145 lbs., height 5 ft. 8.5 in.) is slightly above 3000 cal. daily. The energy requirement of a man varies, with the work performed, between 2500 and 5000 cal., the food requirement between 2750 and 5500 cal. During exposure to a low temp., extra cal. should be supplied, as protein (meat and fish) to a sedentary individual, as fat to a man engaged in bodily work. The av. working woman has an energy requirement of 2400 cal. or a food requirement of 2650 cal.; women engaged in sedentary occupations (such as typewriting) and free from the heavier duties of the home have an energy requirement not exceeding 1900 cal., amply satisfied by a food allowance of 2100 cal. Children over 13 yrs. of age have the same food requirements as an adult of the same sex; those under 6 yrs. 50%, those between 6 and 10 yrs. 60%, those between 10 and 13 yrs. 83% of that of an av. man. A growing child, who works with the same energy as an adult working man, requires additional food, say 200 cal. daily. The brain worker requires 2200 to 2600 cal., light and digestible, and contg. a relatively high proportion of protein. A condition of semistarvation, with the food intake reduced to $\frac{1}{3}$ its normal value, reduces the basal metabolism, and is apparently without danger to health even if extended over a period of several months; if extended over a period of several years, the resistance to tuberculosis is greatly reduced. A diet must contain sufficient cal. as well as minimum amts. of proteins, fats, carbohydrates, salts, and vitamins. The protein content of the diet of an av. man should not be less than 70 to 80 g. daily; it should be derived from a mixed diet, and, if possible, include a certain amt. of protein of animal origin; the diet of infants and young children should contain milk as a source of protein. The minimum desirable amt. of fat eaten daily varies with the race; a Japanese soldier requires 20 g., an Italian laborer less than 60 g., people of British descent 75 g., as much as 35 or 40% of the total energy may be supplied as fat; in vigorous muscular effort at least 25% of the food energy should be represented by fat. To supply vitamins, a certain proportion of fresh fruits or green vegetables should be included in the diet.

JOSEPH S. HEPBURN

Studies in animal nutrition. II. Changes in proportions of carcass and offal on different planes of nutrition. C. R. MOULTON, P. F. TROWBRIDGE, AND L. D. HAIGH. Univ. Missouri Agr. Expt. Sta., *Research Bull.* No. 54, 76 pp. (1922).—III. Changes in chemical composition on different planes of nutrition. *Ibid.* No. 55, 82 pp. (1922). Cf. C. A. 16, 431.

H. B. LEWIS

Physiological criticism of basal metabolism. JULES LEFÈVRE. *Bull. soc. hyg. aliment.* 10, 595-617 (1923).—From a detailed discussion L. draws the following conclusions: So-called basal metabolism has no right to this title because it has no basal characteristics. By attributing to fast and to abs. rest an importance which they do not possess, the authors of basal metabolism lured themselves into believing that they were dealing with basal phenomena, when as a matter of fact they were far from any true base because they neglected to eliminate the preponderating influence of the surrounding temp. The true basal metabolism can be found only by attaining strict thermal neutrality. This can be obtained by immersing the subject in water at 36° (35-39° according to the normal temp. of the subject). The realization of this thermal neutrality in air is *a priori* indeterminate and chimerical. If the limiting temp., which defines thermal neutrality in air, is not known, and if the metabolism is detd. at some arbitrary

temp., the result obtained would not be the basal metabolism, nor would it bear a fixed relationship to the latter. A. P.-C.

Preventive infant feeding—its simplification. H. J. GERSTENBERGER. *Am. J. Pub. Health* 13, 185-95(1923).—G. considers the nature, prepn., and preservation of foods for preventive infant feeding. NATHAN VAN PATTEN

ABNORMAL

The pathogenesis of rickets. R. PRITCHARD. *Proc. Roy. Soc. Med.* 16, Sect. Dis. Children, I-9(1922).—A resumé, leading to the conclusion that all forms of mal-nutrition lead to acidosis, "status calciprīvus," and rickets. A. T. CAMERON

Critical study of two cases of rickets developing in breast-fed infants. ALAN BROWN, A. M. COURTNEY, F. F. TISDALL, AND I. F. McLACHLAN. *Arch. Pediatrics* 39, 559-68(1922).—Two cases of rickets, one accompanied by tetany, occurred in breast-fed infants. The diet of the mothers during lactation lacked vitamins and certain inorg. constituents required for normal development of the child. The breast milks were abnormal in their ash content; one showed a low Ca content and high K and P content; the other was low in Ca and P. The blood sera of the babies had an abnormal concn. of Ca and inorg. P; in that of one baby Ca was very low; in that of the other baby P was markedly decreased. JOSEPH S. HEPBURN

A dental aspect of nutritional diseases in Central Europe. MICHAEL EPSTEIN. *Dental Cosmos* 65, 155-6(1923).—Intermediate and secondary hemorrhage following the extn. of teeth has been noted in a large number of patients who have been on a diet deficient in vitamins and proteins. JOSEPH S. HEPBURN

DOCKER, F. E. MACDONALD: Diet Essential to Health. The Value of Vitamins. London: Research and Information Bureau. 20 pp. 6s.

F—PHYSIOLOGY

ANDREW HUNTER

The colloidal state of matter. W. J. YOUNG. *Chem. Eng. Mining Rev.* 15, 128-30 (1922).—The role of colloids in physiology is described. C. C. DAVIS

Residual nitrogen. R. GAUVIN. *Bull. sci. pharmacol.* 29, 314-20(1922).—Residual N is the difference between total non-protein N and urea N. It averages 15-20% in urine and 44% in blood plasma. A general discussion of residual N and a review of the methods of detn. are given. For a clinical interpretation of residual N it is necessary to know the method of detn. and the method of expressing it in the clinical report. F. S. HAMMETT

Reductions, oxidations and a linked reaction in the intermediary metabolism of the animal organism. F. KNOOP. *Biochem. Z.* 127, 200-9(1922).—A brief discussion of the mechanism of reductions and oxidations in living material followed by exptl. data, which indicate that the amino acids go over to the imino (or hydroxylamino) acids and these react with pyruvic acid. The pyruvic acid is oxidized to acetic acid while the imino acid is reduced back to the amino acid, and both mols. then give rise together to acetylaminic acid. This synthesis is a linked reaction in which the reduction product and the reduction means are well defined, and which can actually be conceived as a process of physiol. reduction in the animal body. The probability that this is a means of reduction of acidity through the change from the strong pyruvic acid to the weak acetic acid and the coupling up with the N compd. is also discussed. F. S. HAMMETT

Studies on the coagulation of the blood. II. Thrombin and antithrombins. J. W. PICKERING AND J. A. HEWITT. *Biochem. J.* 16, 587-98(1922); cf. *C. A.* 16, 1456, 3507.—Relatively large doses of thrombin can be injected into cats respiring air and with the liver out of circulation without causing intravascular coagulation. The subsequent

injection of a lethal amt. of CaCl_2 fails to induce thrombosis. The blood shed after the injection of thrombin into animals deprived of hepatic activity coagulates much more rapidly than the normal blood of the same animal under otherwise similar conditions. The expts. are directly opposed to Howell's view (A Text-Book of Physiology, 466, 469 (1918); cf. C. A. 13, 1479) that the injection of thrombin stimulates the liver to secrete an excess of antithrombin, which latter neutralizes the injected thrombin and so maintains the fluidity of the blood. They also differ with Howell's suggestions (C. A. 6, 2083) "that prothrombin or thrombin itself constitutes a hormone which excites the secretion of antithrombin," and are concordant with the fact that the typical action of "peptone" on blood can be obtained in cats deprived of hepatic activity. The theories of Morawitz (*Beitrage* 5, 133(1904)) and Fuld and Spiro (*Beitrage* 5, 174(1904)) are also questioned. In their hypotheses the formation of thrombin from thrombogen (prothrombin) is said to be the prelude of the actual coagulation of the blood. Thrombin, they claim, acts directly on the fibrinogen of the plasma causing clotting. So long as it was reasonable to assume that the liver secreted sufficient antithrombin to neutralize the effect of massive doses of thrombin these theories remained tenable; but as large amts. of thrombin can be injected without thrombosis into the circulation when such hepatic secretion is impossible the view that thrombin acts directly on the fibrinogen of *unaltered* plasmas must be discarded. Bordet (C. A. 15, 888) maintains that contact of the blood with foreign bodies causes the interaction of lipoidal cytozyme (thromboplastin), formed largely from platelets but also from leucocytes and other sources, with serozyne, a product of the plasma formed immediately prior to coagulation. Serozyme and cytozyme are then said to combine, in the presence of Ca, to yield thrombin, which in turn acts on fibrinogen to give clots of fibrin. The evidence in the present paper shows that if the phys. conditions of the blood are preserved by remaining in the living vessels, then thrombin, in amts. sufficient to cause coagulation *in vitro*, does not cause thrombosis *in vivo*. It appears, therefore, that although Bordet is correct in assigning importance to the surface conditions of the blood in the maintenance of fluidity, it is not to the disintegration of formed elements yielding thrombin, under the influence of phys. change, that the inception of coagulation is due, but rather to phys. change destroying the stability of the clotting complexes of the plasma. Thrombin should be regarded as an accelerator rather than an initiator of coagulation. No direct evidence has been obtained of the existence of antithrombin in *living* animals. The employment of Doyon's technic (C. A. 15, 2116, 3294; 16, 1104 antithrombin and *Arch. Intern. Physiol.* 16, 343(1921)) for prep. antithrombin from liver, yielded from yeast an ext. which exhibited the properties of antithrombin. The hydrolysis of edestin also gave an anticoagulant. It is concluded that antithrombins are not phylogenetic products of the animal kingdom arising late in evolution as a protection against thrombosis, but are products resulting from the hydrolysis of proteins.

BENJAMIN HARROW

Does thiocyanic acid have any function in the animal organism? E. CAVAZZANI. *Arch. fisiol.* 18, 93-5(1920); *Physiol. Abstracts* 6, 405(1921).—In approx. physiological concns., HCN prevents the peptic digestion of fibrin. JOSEPH S. HEPBURN

Physiological study of two Thiry intestinal fistulas in a dog. A. D. VOLTA. *Arch. fisiol.* 18, 97-134(1920); *Physiol. Abstracts* 6, 432-3(1921).—Thorough examn. was made of 2 Thiry fistulas which had existed on the same dog for 5 years. The isolated intestinal segments were functionally and anatomically normal; and their hind ends were characterized by regenerative phenomena extending to the mucous, submucous and muscular coats without leaving any scar or trace of the operation. JOSEPH S. HEPBURN

Secretion of bile in man. B. BRUNACCI AND U. NOFERI. *Arch. fisiol.* 18, 135-51, 153-65(1920); *Physiol. Abstracts* 6, 433.—The study was made on a woman, 60 years of age, upon whom cholecystostomy had been performed 2 months previously. When

the patient fasted but received an unlimited supply of water by mouth, bile was continuously secreted in an amt. but slightly less than that produced after carbohydrate meals. Ingestion of fats and of proteins was followed by an abundant secretion of bile. During fasting, the amt. of bile increased slowly during the first few hours of the day, attained a max. after 12 to 16 hrs., then declined progressively to the end of the 24th hr. When food was ingested, the max. secretion usually occurred shortly after eating and within 4 hours. The influence of ingested fat on the secretion of bile ended within 24 hours, that of ingested proteins continued over the next day. The vol. of ingested water apparently did not influence the amt. of bile secreted. During fasting, and during a mixed diet, the elec. cond. and mol. concn. of the secreted bile showed but small oscillations; their max. and minimum points were attained sooner after eating than after fasting; on a mixed diet, they ran parallel to the body temp. in a striking manner. The cryoscopic point and elec. cond. of the bile yielded minimum values on an exclusively protein diet, and max. values after the ingestion of fats or sugar or after fasting. The elec. cond. of the urine increased with its sp. gr. The viscosity of the secreted bile was least after ingestion of protein food, greatest after fasting; the total solids (dtd. at 100°) were greatest after a carbohydrate diet, while the ash content was greatest after a protein diet and after fasting; the N content was always small. The amt. of indican excreted was related to the total N of the urine; and the bile probably has no influence on intestinal putrefaction.

JOSEPH S. HEPBURN

Action of gustatory stimuli on the rate of secretion of human parotid saliva, and on its diastatic power. T. DE SANTIS-MONALDI. *Arch. fisiol.* 18, 168-70(1920); *Physiol. Abstracts* 6, 432(1921).—Various stimuli (bread, meat, acid) accelerate the secretion of human parotid saliva. Apparently none of the usual stimuli influences the diastatic power of this saliva.

JOSEPH S. HEPBURN

Anatomical modification of the spleen after thymectomy. G. BAGGIO. *Arch. fisiol.* 19, 290-315(1921); *Physiol. Abstracts* 6, 639-40(1922).—Thymectomy was performed on rabbits from 20 to 80 days old. As a result, the spleen decreased in wt., on the av., 182 mg. or 78%, but did not show any histological changes. The body wt. decreased in 62.5% of the exptl. animals.

JOSEPH S. HEPBURN

Significance of the structures occurring in the protoplasm and without the nucleus of gland cells. H. LUTZ. *Arch. Zellforsch.* 16, 47-57(1921); *Physiol. Abstracts* 7, 12(1922).—Conclusions are drawn from observations made on the glands of the mesenteron of *Planorbis corneus*. Both the nucleus and the cytoplasm participate in the work of secretion. The activity of the nucleus is shown by changes in its size and chromatin content; formation of chromidia does not occur. The activity of the cytoplasm is shown by the mitochondria and the basophile structures; the latter form the true secretion and contain a compd. resembling nucleic acid; the mitochondria are not permanent cell organs, but are formed anew for each period of activity. J. S. H.

Functional coordination in the digestive canal. E. ZUNZ. *Bull. soc. roy. sci. méd. natur. Bruxelles* 1921, 55-78; *Physiol. Abstracts* 6, 372-3(1921).—In order to insure functional coordination, the organism has both a nervous and a chem. or humoral regulatory mechanism. Thus relationships exist, in the case of the digestive tract, between (1) the motor activity of the fasting stomach, hunger, and appetite, (2) the secretion of the digestive juices and the presence in the food of substances which stimulate their secretion either directly or indirectly, and (3) intestinal peristalsis and choline. A résumé is given of the various functional interrelations.

JOSEPH S. HEPBURN

Aqueous extracts do not contain prothrombin. P. NOLF. *Compt. rend. soc. belge biol.* 1921, 1116-8; *Physiol. Abstracts* 7, 27(1922).—An aq. ext. prepd. from a heart, which has continued beating during perfusion with Ringer soln. for more than an hr. after its removal from the body, entirely lacks coagulating action upon a soln. of fibrinogen, but rapidly coagulates plasma.

JOSEPH S. HEPBURN

Plasmas agglutination, a factor in the instability of particles introduced into the circulation. P. GOVAERTS. *Compt. rend. soc. belge biol.* 1921, 244-5; *Physiol. Abstracts* 6, 393(1921).—Certain constituents of India ink are perfectly stable in dog serum, but are immediately agglutinated if added to a pure plasma containing 1% of oxalate. Staphylococci behave in a similar manner. Plasmas agglutination may remove from the blood microorganisms which are introduced into the circulation. J. S. H.

Influence of substances extracted from the heart of the turtle on the heart of the frog. J. DEMOOR. *Compt. rend. soc. belge biol.* 1921, 1091-3; *Physiol. Abstracts* 7, 33.—The isolated frog heart is not modified in its action on perfusion with Ringer soln. to which the aq. ext. of frog heart has been added. The same heart, subjected under the same conditions to the action of the ext. of turtle heart, shows a decrease in both inotropism and chronotropism; substitution of Ringer soln. as the perfusing liquid restores the heart to its normal movement. The ext. of ordinary muscular tissue of the turtle is very toxic for the turtle heart, producing a decrease in both inotropism and chronotropism. These results tend to prove the existence, in the turtle heart, of sp. substances which stimulate the movement of the frog heart and impart to it a new, special rhythm. JOSEPH S. HEPBURN

Influence of substances extracted from the auricles and the ventricles of the dog heart on the isolated rabbit heart. J. DEMOOR. *Compt. rend. soc. belge biol.* 1921, 1093-5; *Physiol. Abstracts* 7, 33.—Perfusion of the isolated rabbit heart with Locke soln. contg. glucose and enriched with an ext. obtained by maceration of the auricles of the dog for 30 hrs. produces a marked inotropism (amplification of the contractions or increase in tonus) and a more rapid chronotropism. These reactions persist as long as the heterogeneous ext. is perfused, and disappear when simple Locke soln. is used. The ext. of the ventricles of the dog, in general, has a depressant action on the work of the heart, which continues to beat regularly but more slowly and less strongly than when perfused with Locke soln. The ext. of ordinary dog muscle often is without action, but sometimes is very plainly toxic. The auricles and the ventricles of the dog contain sp. substances having very distinct, special action on the rabbit heart. J. S. H.

Peculiar eosinophiles in the dog. D. ZIBORDI. *Hematologica* 1, 451-3(1920); *Physiol. Abstracts* 6, 182(1921).—The leucocytes in the bone marrow, spleen, and circulating blood of dogs infected by *Tuonia cucumeria* contained uncommonly large eosinophilic granules. This phenomenon supports the view that these granules originated from ingested particles of fragmented erythrocytes. JOSEPH S. HEPBURN

Observations on erythrocytes treated with potassium permanganate. L. SABATANI. *Hematologica* 1, 485-506(1920); *Physiol. Abstracts* 6, 494(1921).—When a suspension of rabbit erythrocytes in a physiol. soln. is mixed with an isotonic KMnO_4 soln., their colloidal org. matter is destroyed by oxidation and is replaced by brown colloidal MnO_2 , which forms as a sol but passes into a gel so that the cells are almost unaltered in form. The MnO_2 forms first in regions where the org. matter either is accumulated in greater quantity or is more avid for O. Since rabbit erythrocytes yield a uniform brown color, this reaction fails to show any differentiation within them. J. S. H.

Formation of endoglobular pseudonuclei and Cabot's rings as shown in normal erythrocytes with hypercoloration. A. C. DEMEL. *Hematologica* 2, 125-46(1921); *Physiol. Abstracts* 6, 494-5(1921).—Histochem. study shows that the erythrocytes are not homogeneous, and that both the nucleoid endoglobular formations and Cabot's rings are normal. JOSEPH S. HEPBURN

Role of hydrogen- and hydroxyl-ion diffusion in nerve and muscle action. E. Q. ADAMS. *J. Phys. Chem.* 26, 639-46(1922).—Calculs. have been made, based on the assumptions that nerve and muscle action depend on an autocatalytic conversion of glucose or galactose to lactic acid, kept in check by diffusion, and that the significant

factors in the initiation of a response are this autocatalytic reaction and the diffusion of the H ion and the OH ion. In plasma with the reaction of normal blood (p_H 7.35), the reaction within the excitable nerve or muscle fiber lies between p_H 7.29 and p_H 6.99. For effective stimulation, the reaction must be acidified locally within the fiber to a critical value, which depends on the concn. of enzyme (lactacidase) present in the fiber, and must have a $p_H < 6.99$. The response of nerve or muscle will be abolished by a plasma reaction of p_H 6.92; this fact is in agreement with the observation that the most acid reaction during life is p_H 6.95, occurring in deep coma. J. S. H.

Colostrum. III. E. BRUGNATELLI. *Pathologica* 13, 368-71(1921); *Physiol. Abstracts* 7, 55(1922).—Diastase is present, and may be detected by means of the Wohlgemuth method in as little as 0.1 to 0.2 cc. of colostrum. JOSEPH S. HEPBURN

Significance of the concentration of calcium ions for the movements of the stomach caused by stimulation of the vagus nerve. R. BRINKMAN AND E. VAN DAM. *Proc. Acad. Sci. Amsterdam* 23, 1262-70(1922).—By expts. similar to those previously noted (cf. C. A. 15, 2918), it is shown that a decrease in the HCO_3 anion can cause spastic contraction of the stomach and an increased irritability of the vagus nerve (vagotonia).

JOSEPH S. HEPBURN

Characteristic effects upon growth, estrus, and ovulation induced by the intraperitoneal administration of fresh anterior hypophyseal substance. H. M. EVANS AND J. A. LONG. *Proc. Nat. Acad. Sci.* 8, 38-9(1922).—Intraperitoneal administration of finely ground fresh anterior lobe of the hypophysis of beef caused rats to become much heavier than their litter mate sisters; a certain degree of true gigantism was produced; the skeleton, heart, lungs, kidneys, alimentary canal, and fat deposits in the omentum and mesentery were heavier in the exptl. animals than in their controls; the wt. of the thymus, thyroid and hypophysis was not appreciably influenced. Estrus occurred rarely, if at all, in the exptl. animals; their ovaries had twice the normal weight and contained larger nos. of corpora lutea; the uterus had approx. one-half its normal wt. A powerful sp. stimulus to lutein cell transformation in the gonads had been exerted by the anterior hypophyseal substance. Fresh posterior hypophyseal substance was tolerated in smaller amts., but produced none of these characteristic changes in growth, estrus, and ovulation.

JOSEPH S. HEPBURN

Glycogen in the nerves of the auricle. P. ROJAS. *Rev. ibero-amer. cienc. med.* 44, 110-6(1920); *Semana med.* 27, 591-5(1920); *Physiol. Abstracts* 6, 554-5(1922).—Stained preps. demonstrated the abundance of glycogen in the Purkinje tissue. In the fetal heart, the glycogen content of these cells was the same as that of the general myocardial fibers.

JOSEPH S. HEPBURN

Preservation of food by freezing with special reference to fish and meat; a study in general physiology (STULES). 12.

HÄRL, PAUL: *Kurzes Lehrbuch der physiologischen Chemie*. 2nd revised Ed. Berlin: Julius Springer. 353 pp.

G—PATHOLOGY

H. GIDEON WELLS

The cortex of the adrenals in the course of antidiphtheric vaccination and of diphtheric toxemia. CLEVERS AND GOORMAGHTIGH. *Bull. acad. roy. med. Belg.* [5] 2, 425-38(1922).—A microscopic examn. of the localization of cholesterol and its esters in the cortex of the adrenal of guinea pigs after injection of diphtheria toxin and antitoxin shows that the esters of cholesterol are accumulated in the normal state in a narrow layer of the cortex while, after toxin injection, they are distributed over a somewhat wider region for a definite period. The excretion of a lipoproteic substance is considerably increased during that time. The total quantity of cholesterol in the adrenal increases,

a part of it being discharged into the blood. In *diphtheric toxemia* cholesterol is also discharged into the blood while similar changes occur in the adrenal. R. BEUTNER

The connection between lipid metabolism and hemolytic anemia. J. GOUDSMIT. *Nederland. Tijdschr. Geneeskunde* 66, II, 1398-1408(1922).—According to Brinkman (*Nederland. Tijdschr. Geneeskunde* 66, I, 2462(1922)) hemolytic anemia can originate if the ratio lecithin : cholesterol is increased. According to others abnormal products of decompn. of lecithin may produce hemolysis *in vivo*. The change of the lipid metabolism is due to pathological resorption from the intestines. R. BEUTNER

Further clinical experience with insulin (pancreatic extracts) in the treatment of diabetes mellitus. F. G. BANTING, W. R. CAMPBELL AND A. A. FLETCHER. *Brit. Med. J.* 1923, I, 8-12.—The most striking results have been seen in children and young adults, but all patients have benefited. If sufficient insulin is given the urine becomes sugar-free on the 1st or 2nd day and ketone-free on the 2nd or 3rd. Ten cases of complete coma have been treated. One is now aglycosuric without insulin on a diet double the basal requirement; 5 remain free from symptoms with no glucosuria nor ketonuria on diet treatment plus insulin. Over-dosage of insulin in man leads to hypoglycemia with symptoms of hunger (at about 0.07% blood sugar), "nervousness," and with still lower sugar values sometimes a definite neurosis, difficulty of articulation, and, always, with sufficiently low value (order of 0.03%), coma. These symptoms can be removed by food administration (5s to 25 g. glucose with orange or lemon juice) or, if the patient is unconscious, 1 cc. adrenaline (1 in 1000) intramuscularly, followed by glucose by mouth or in extreme cases intravenously. A. T. CAMERON

Insulin, diabetes, and rewards for discoveries. W. M. BAYLISS. *Nature* 111, 188-91(1923).—The first part is a description of Banting *et al.*'s work (*C. A.* 17, 580, 1054 and preceding abstr. on "insulin." The second deals with rewards in the field of pure research. BENJAMIN HARROW

A possible mode of causation of diabetes mellitus. L. B. WINTER AND W. SMITH. *Brit. Med. J.* 1923, I, 12-3; cf. *J. Physiol.* 57, 100(1922).—Sols. of glucose or fructose incubated at 37° with very small amts. of insulin and liver ext. in a jacketed polarimeter tube have their rotations altered in a downward and an upward direction, resp. Addn. of phosphate accelerates the action to a degree not obtained by use of other salts. Boiled liver ext. is inactive. Insulin is thermostable in this respect. The sugar formed (γ -glucose?) is unstable; after the max. change has occurred the rotation tends to return to the original value. Since the sugar is not removed from the sphere of action no marked amt. is formed. The insulin obtained by Collip's method is capable of being divided into 2 fractions which differ markedly in their nature and activity as tested by the above method and on rabbits. A. T. CAMERON

Triple test of renal permeability by fluorescein, methylene blue and free iodine. ED. CROUZEL. *Repert. pharm.* 35, 1-3(1923).—The use of one reagent as a test for the permeability of the kidney is not sufficient for clinical purposes. It is proposed to give 1-g. doses of methylene blue, fluorescein and KI on 3 successive days. A colorimetric detn. of the amt. of these substances in the 24-hr. sample of urine is made to det. the % excreted. A. A. CHRISTMAN

Changes in the dissociation curve of the blood in experimental fever and febrile diseases. M. YAMAKITA. *Tohoku J. Exptl. Med.* 2, 290-323(1921); *Physiol. Abstracts* 6, 598.—Pyrexia induced by puncture of the corpus striatum or injection of peptone, Koch's old tuberculin, or typhoid toxin is accompanied (with some individual exceptions) by a decrease in the % satn. of the blood with O₂. The relation between fever and acidosis is not strictly parallel, but is approx. so after typhoid toxin injection. During the febrile periods of phthisis, influenzal pneumonia, and typhoid fever, acidosis is also present. The acidosis is attributed partly to tissue disintegration and partly to

the rise of body temp. itself. Injection of Na_2CO_3 improves the % O_2 satn. of the blood in animals with fever, and may do so in febrile diseases of man. H. G.

Standardization of botulinus antitoxin. I. A. BENGTSON. *Abstracts Bact.* 5, 25-6(1921).—Botulinus antitoxin is tested and standardized by a procedure similar to that used for tetanus antitoxin. Standard serums and dried toxins of both Types A and B are used, serum and toxin of the same type being tested against each other. The antitoxin unit just fails to neutralize 1000 min. lethal doses of the original toxin. The toxin used in the test is first compared with the standard antitoxin to ascertain the test dose. Then the number of units in the unknown antitoxin are detd. by titration against the test dose of toxin. JOSEPH S. HEPBURN

Diet as a factor in the cause of rickets. LEONARD FINDLAY. *Arch. Pediatrics* 38, 151-62(1921).—Exptl. and clinical evidence scarcely justifies the classification of rickets as a deficiency disease. Treatment of rachitic children by means of massage and electricity was found a far better curative procedure than control of the diet and administration of cod-liver oil and phosphorated oil. JOSEPH S. HEPBURN

Hemolysis and fixation with ethyl alcohol; comparative hemolytic and fixative action of metals. E. MENEGHETTI. *Arch. sci. biol.* 2, 279-317(1921); *Physiol. Abstracts* 7, 56(1922).—Hemolysis is probably due to relationships of soly. between alc. and the lipins of the erythrocytes, while fixation depends upon relationships between alc. and their proteins. The action of metallic salts upon erythrocytes depends on the concn. and activity of the cations; the hemolytic action increases in the following order $\text{Zn} < \text{Cd} < \text{Fe}, \text{Co} < \text{Ni}, \text{Pt} < \text{Pb} < \text{Cu}, \text{Hg}, \text{Pd} < \text{Au} < \text{Ag}$. Extremely small amts. of metals suffice to produce hemolysis. Usually the hemolytic and fixative actions of metallic salts become more intense as the tension of the soln. of the cation decreases. JOSEPH S. HEPBURN

Mode of action of formaldehyde on organic colloids. I. Role of formaldehyde in the prevention of the reactivity of luetic sera. H. KÜRTEN. *Biochem. Z.* 133, 128-36(1922).—Various concns. of HCHO act upon pure undild. serum and upon plasma to produce an increase in viscosity; the HCHO gives rise to a change in the proteins which are present in the serum and react in a characteristic manner with the lipins of the ext. (antigen). HCHO has practically no action on suspensions of these lipins (cholesterol and lecithin); a very slight tendency to increase their suspensoid nature is sometimes noted. The changes in the serum globulins in syphilis probably explain the action of HCHO upon syphilitic sera. JOSEPH S. HEPBURN

Platelets and bleeding time. II. J. ROSKAM. *Compt. rend. soc. belge biol.* 1921, 18-20; *Physiol. Abstracts* 6, 310(1921).—In the dog, the decreased coagulability of the blood, which is produced by sudden injection of gelatin or by injection of ext. of leech heads, markedly increases the coagulation time. The ext. of leech heads probably prevents the adhesion of the platelets to the edges of the wound. The gelatin gives rise to a marked decrease in the platelet count. Since the blood is not coagulable, the platelets are unable by themselves to close a vascular wound efficaciously. J. S. H.

Influence of small doses of peptone upon the elimination of microorganisms injected into the circulating blood. E. DELCOURT-BERNARD. *Compt. rend. soc. belge biol.* 1921, 238-40; *Physiol. Abstracts* 6, 566(1922).—Peptone, in small doses, decreases the affinity of the platelets for each other. If the platelets have a part in the elimination of microorganisms, the elimination is independent of the vol. of the aggregates of the platelets. The 2 phenomena (aggregation of the platelets and union of the aggregates with the microorganisms) are not necessarily parallel. Peptone, in small doses, promotes phagocytosis in the blood of the rabbit and of the guinea pig. JOSEPH S. HEPBURN

Influence of antiplatelet serum upon the toxic effects of serum treated with agar. E. ZUNZ AND P. GOVAERTS. *Compt. rend. soc. belge biol.* 1921, 248-51; *Physiol. Abstracts*

6, 393(1921).—Intraperitoneal injection of antiplatelet serum, 24 hrs. previously, slightly decreases the harmful effects which follow the introduction into the guinea pig of serum treated with agar. JOSEPH S. HEPBURN

Antiforeign function of the platelets. J. ROSKAM. *Compt. rend. soc. belge biol.* 1921, 269-71; *Physiol. Abstracts* 6, 367(1921).—The union of the platelets with foreign particles in the presence of the plasma is a passive phenomenon independent of the life of the platelets. This fact may be verified by use of either (1) an emulsion of platelets, killed by heat, in distd. water or NaF or (2) turbid plasma heated for 1.5 hrs. at a temp. of 48° to 50°. JOSEPH S. HEPBURN

Antiforeign power of the platelets. J. ROSKAM. *Compt. rend. soc. belge biol.* 1921, 733-5; *Physiol. Abstracts* 6, 566(1922).—A gradual increase in the temp. first decreases, then destroys the agglutinating power of the plasma (pptn. and alteration of certain of its proteins) and of the isolated washed platelets on particles of India ink. Repeated washings of the platelets with physiol. NaCl soln. progressively decrease their agglutinative power on these particles. These facts indicate that the agglutinative power of the organism resides in the plasma; the platelets participate by virtue of the coating of plasma on their surface. JOSEPH S. HEPBURN

Researches on the antigenic principle of the erythrocyte. F. CHODAT. *Compt. rend. soc. belge biol.* 1921, 735-8; *Physiol. Abstracts* 6, 566(1922).—The stroma itself and not the globulins forms the antigen extd. from erythrocytes by distd. water contg. CO₂. This antigen reacts with the immune bodies of hemolytic sera. JOSEPH S. HEPBURN

Effect of the injection of washed platelets upon the elimination of bacteria circulating in the blood. P. GOVAERTS. *Compt. rend. soc. belge biol.* 1921, 745-7; *Physiol. Abstracts* 6, 566(1921).—One-half hour after injection of *B. typhosus* into the veins of a guinea pig, the number of bacteria present in the circulation decrease continuously but slowly. If washed platelets be then injected into the veins, a very marked decrease occurs in the number of bacteria. This decrease is not produced by injection of a suspension of washed erythrocytes. JOSEPH S. HEPBURN

Coagulation of the cerebrospinal fluid in three cases of medullary compression. P. GOVAERTS. *Compt. rend. soc. belge biol.* 1921, 748-50; *Physiol. Abstracts* 6, 564(1922).—The 3 fluids were poor in cells but rich in protein which did not coagulate spontaneously but coagulated on the addition of fresh serum. Lack of spontaneous coagulation apparently was due not to the presence of antithrombin, but to lack of cytozyme, since addition of the latter produced coagulation. Certain exudates of the serous membranes and articulations behave in the same manner. JOSEPH S. HEPBURN

Reaction of Hecht in pregnancy. M. WATRIN. *Compt. rend. soc. biol.* 85, 264-5 (1921).—The serum reaction of Hecht for syphilis may be applied to gravid serum; the fetal blood contains complement but no antihody. Blood from the umbilical cord never contains the placentalolytic protective enzyme of Abderhalden which is always present in the maternal blood. The autolytic power and the power to activate hemolysis by cobra venom are always less in the blood of the cord than that of the mother. Hypercholesterolemia is always present in the mother, hypocholesterolemia always in the cord blood. JOSEPH S. HEPBURN

Action of chloroform upon inactive serum. P. NOLF. *Compt. rend. soc. biol.* 85, 268-9(1921).—If sterile rabbit serum be kept for 2 or 3 days at a temp. of 37°, it loses its power to coagulate fibrinogen and has a distinct inhibitive action on the coagulation of that protein by thrombin. If such inactive serum be subjected to the action of CHCl₃ for 1 or more hrs. at a temp. of 37°, the coagulating power returns and the antithrombic action disappears; this is true even if the CHCl₃ be evapd. By the action of the CHCl₃, thrombin is formed from the parent substance present in the inactive serum. Therefore, in the coagulation of plasma, all the parent substance of thrombin is not transformed into the active enzyme. JOSEPH S. HEPBURN

Two cases of sialolithiasis. F. A. KEYES. *Dental Cosmos* 65, 49-50(1923).—Two cases of salivary calculus are reported, one from Wharton's duct, the other from the submaxillary gland. JOSEPH S. HEPBURN

Certain factors causing the deposition of lime salts in bone. E. A. PARK. *Dental Cosmos* 65, 176-85(1923).—Description of the factors governing the development and the prevention of rickets. JOSEPH S. HEPBURN

Wassermann test in pregnancy. S. W. SAPPINGTON. *Hahnemannian Monthly* 58, 90-7(1923).—The test was applied to 1300 pregnant women, white and colored being fairly evenly divided; 5.4% of the whites and 18.3% of the blacks gave a positive result (3 plus or 4 plus) with 3 antigens and ice-box incubation. JOSEPH S. HEPBURN

Formation of antibacterial substances in the blood in vitro. R. PAOLUCCI. *Hematologica* 1, 523-39(1920); *Physiol. Abstracts* 6, 529(1921).—Bacterial vaccines cause antibacterial properties to appear in blood which is removed from the influence of the tissues. These properties are probably bactericidal; they are non-specific and thermolabile. JOSEPH S. HEPBURN

Calcium content of blood serum in pregnancy and childbirth. P. MAZZOCO AND R. BUSTOS MORON. *Compt. rend. soc. biol.* 85, 692(1921).—The Ca content of the blood serum in pregnancy and childbirth is only slightly below normal, namely 8.77-8.79 mg. per 100 cc. as against 9.19 mg. per 100 cc. in normal sera. The Ca content of the serum is thus of no diagnostic value for pregnancy. No correlation can be shown between the fall in serum Ca and the development of pregnancy and its related maladies. J. C. S.

Uric acid content of blood corpuscles. A. CHAUFFARD, P. BRODIN, AND A. GRIGAUT. *Compt. rend. soc. biol.* 86, 31-2(1922).—The uric acid content both of blood serum and of blood corpuscles is twice as great in gouty conditions as in normal health. In the former case, the uric acid content of the corpuscles bears a more constant relationship to the uric acid content of the serum than in the latter case (cf. Theis and Benedict, *C. A.* 16, 118). J. C. S.

Periodicity in chloride excretion during dropsical nephritis. P. L. VIOLLE. *Compt. rend. soc. biol.* 86, 362-3(1922).—In dropsical nephritis with marked retention of chlorides, the excretion of NaCl is const., independently of the water balance. When the kidneys again become permeable to chlorides, variations in the daily output of chlorides occur. J. C. S.

Effect of ether on antibodies. J. FORSSMAN. *Compt. rend. soc. biol.* 86, 495-7(1922); cf. *C. A.* 16, 2908.—When heated with Et_2O at 50° , hemolysin is destroyed while agglutinin is unaffected. Protective antibodies behave normally. With sera, varying results are obtained owing to the presence of protective colloids. To this may be attributed the fact that antibodies pptd. by $(\text{NH}_4)_2\text{SO}_4$ behave differently from those pptd. by AcOH and distd. water. J. C. S.

Organic acids in urine. R. GOIFFON AND F. NEPVEUX. *Compt. rend. soc. biol.* 86, 1132-3(1922).—By using the method of Van Slyke and Palmer (*C. A.* 14, 1689), the authors found in cases of acetonuria increase in total org. acids and in β -hydroxybutyric acid in the urine. Sufficient agreement was not obtained for these acids to be regarded as the sole factor in acetonuria. The org. acid content is independent of the acidity. NaHCO_3 renders the urine alk. without diminution in the org. acid content. J. C. S.

Tests for liver function. LEPPNE. *Munch. med. Wochschr.* 69, 342-4(1922).—Hay's flowers of sulfur test for bile acids in duodenal juice and urine is described in application to certain pathological conditions. J. C. S.

Cholesterol in cerebrospinal fluid. STANISLAO FABRIS. *Pediatrics* 29, 1057-64(1921).—In normal children, 0.01% of cholesterol was found in cerebrospinal fluid. In hydrocephalic cases, cholesterol was absent, while in tubercular meningitis increased amts. were found. J. C. S.

Adrenaline hyperglucemia. CH. ACHARD, A. RIBOT, AND LÉON BINET. *Rev. med.* **38**, 447-56(1921); cf. *C. A.* **16**, 4264.—The percentage increase in blood sugar and its duration depend on the amt. of dextrose injected. With injection of dextrose and adrenaline, hyperglucemia is more pronounced. Hypophysis ext. exerts the same effect. With dextrose and aq. pancreatic ext., the hyperglucemia is less than with dextrose alone. Pancreatic ext. partly neutralizes the effect of adrenaline in adrenaline hyperglucemia.

J. C. S.

Sugar regulation in paralysis agitans. K. DRESEL AND F. H. LEWY. *Z. ges. expul. Med.* **26**, 95-103(1922).—After administration of sucrose in paralysis agitans, blood sugar remains normal for 1.5 hrs., but ultimately rises above the normal. After administration of dextrose, blood sugar remains longer at a max. than in normal cases.

J. C. S.

Studies on sugar tolerance. R. H. MAJOR. *Bull. Johns Hopkins Hosp.* **34**, 21-6(1923).—The glucose tolerance test was carried out on 60 patients suffering from diabetes mellitus, renal glucosuria, nephritis, and thyroid and pituitary disease. The observations indicate that as a rule the urine does not show sugar in appreciable amts. until a definite blood sugar level is reached. This level or "renal threshold" varies somewhat in health but markedly in disease. Repeated tests on the same individuals show marked variations in this "renal threshold." Four individuals classed as "renal diabetics" showed glucosuria with a blood sugar at normal or subnormal levels.

A. P. LOTHROP

Enzymes in the duodenal fluid in hyperthyroidism. K. GYOROKU. *Japan Med. World Z.* **339**(1922).—There is no great fluctuation in the amt. of enzymes in the duodenal fluid in the same individual within a short time. 60% of the cases of Grave's disease show a decrease. There is no relation between achylia or hypochlorhydria and the amt. of enzymes present in the duodenal fluid. In those cases with a decreased amt. of enzymes there are marked digestive disturbances. There is no relation between these enzymes and the degree of disturbances of the carbohydrate metabolism.

M. E. MAYER

"Specific viscosity" of blood serum. PAUL SPIRO. *Kolloid Z.* **31**, 345(1922).—Sp. viscosity of blood serum is the relation of the viscosity of a blood serum of known albumin concn. to the viscosity of a normal serum of equal albumin concn. This sp. viscosity of blood serum is more useful to the empirically working technician than viscosity referred to H₂O. An abnormally high sp. viscosity was found in acute and sub-acute infections, exudative tuberculosis, cardiac and renal insufficiencies. Lowering of sp. viscosity was not observed.

A. MUTSCHER

Prevention of pneumonia by pneumococcus vaccine. R. L. CECIL. *Am. J. Pub. Health* **13**, 182-5(1923).—A resumé.

NATHAN VAN PATTEN

D'HERELLE, F.: **The Bacteriophage—Its Role in Immunity.** Authorized English translation by George H. Smith. Baltimore: Williams & Wilkins Co. 287 pp. \$4, U. S., Mex., Cuba; \$4.25, Canada; \$4.50 other countries, net postpaid.

PERÈS, MARIUS: **La réaction du benjoin colloïdal dans le liquide céphalo-rachidien, normal et pathologique.** Toulouse: Impr. E. H. Guillard. 76 pp.

WELLS, H. GIDEON, DE WITT, LYDIA M., AND LONG, ESMOND R.: **Chemistry of Tuberculosis.** Baltimore, Md.: Williams & Wilkins Co. 438 pp. \$5, U. S., Mexico, Cuba; \$5.25, Canada; \$5.50, other countries.

H—PHARMACOLOGY

ALFRED N. RICHARDS

Pharmacology of some phenylenediamines. P. J. HANZLIK. *J. Ind. Hygiene* **4**, 386-409, 448-62(1923).—The pharmacology of *m*- and *p*-C₆H₄(NH₂)₂ and their dimethyl and diethyl-derivs. is studied. Because of their lipid soly. these compds. may be ab-

sorbed through the skin to give toxic effects. Stimulation of circulation, and respiration, fall of body temp., tremors, convulsions, coma and death follow the subcutaneous injection of the compds. into mammals. The injection of $p\text{-C}_6\text{H}_4(\text{NH}_2)_2$ into rabbits produces a characteristic edema of the face, tongue and nose. Workmen in plants using the above diamines should be protected and the use of this group of compds. should be prohibited in the manuf. of hair dyes and cosmetics.

A. A. CHRISTMAN

The action of cyanamide. I. ERICH HESSE. *Z. ges. expil. Med.* 25, 321-44 (1921).—Cyanamide increases the action of such drugs as alcohol, chloral hydrate, NaBr and theohromine. Contrary to statements in the literature, alcohol does not increase the action of cyanamide.

E. B. FINK

The physiological action of the metallic ammoniates and related compounds. AD. OSWALD. *Biochem. Z.* 127, 156-67 (1922).—Frogs, white mice and rats were used in these expts. The action of compds. of the type $[\text{Co}(\text{NH}_3)_3][\text{NO}_3]_2$; $[\text{Co}(\text{NH}_3)_3\text{Cl}]\text{Cl}$; $[\text{Co}(\text{NH}_3)_4(\text{OH})\text{H}_2\text{O}]\text{Br}_2$; $[\text{Cr}(\text{OH})_2\text{Cr}(\text{NH}_3)_4]\text{Cl}_6$; $[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{Na}_3$; $[\text{Cr}(\text{C}_2\text{H}_4\text{-(NH}_2)_3)_3]\text{I}_3$; $[\text{Co}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2(\text{Ac}_2\text{CH}_2)_2]\text{I}_2$; and $[\text{Fe}(\text{C}_2\text{H}_5\text{N}_2)_2]\text{Br}_2$ was studied. In general the metallic ammoniates as well as their substituted compds. give the reaction of the associated radical. They affect the motor centers, first as stimulants, then as paralyzants. Probably org. compds. all act physiologically as referable to a few basic types, such as the methane type, the benzene type, the ammonia type, etc.

F. S. HAMMETT

The increase in the rapidity and intensity of the toxic action of some groups of poisonous or pharmacologically active substances on bacteria and tadpoles by variation of the degree of alkalinity or acidity. A contribution to the question of permeability. R. LABES. *Biochem. Z.* 130, 14-24 (1922).—L. confirmed the findings of other investigators that the addition of Na_2CO_3 to the soln. of an alkaloid salt increases the rapidity and intensity of its toxic action. Further studies showed that the effectiveness depends largely on the p_H of the soln. used. In general an increase in the p_H of the phosphate-buffered solns. brought about an increase in the alkaloid activity. The opposite relations existed when those salts were used which, in contradistinction to the alkaloid salts, depend on the acid radical for their toxic effect; e. g., Na butyrate and benzoate, which are to a high degree changed to lipid-sol. undissociated acids with increasing acidity. These compds. become more rapidly and intensely toxic with increasing acidity. When pharmacologically active substances were used, of which the lipid soly. and surface activity are independent of the p_H , such as acetanilide and ethylurethan, changes in the p_H had no effect on their activity. In the studies with staphylococci the solns. were buffered with Na acetate and acetic acid. The same relations were shown here as with the tadpoles. L. believes that the dependence of the toxic compds. on the p_H in the case of the tadpoles is due to changes in permeability, particularly in the case of the lipid-sol. compds.

F. S. HAMMETT

The secretin action of methyl *N*-methylnipecotate *N*-methochloride. K. HARAKI. *Biochem. Z.* 130, 267 (1922).—"Neu-Cesol," Me ester of *N*-methylnipecotic acid methochloride, has a marked stimulating effect on gastric secretion. F. S. H.

Some factors which modify the adrenaline reaction. J. B. COLLIP. *Endocrinology* 6, 402-7 (1922).—A brief review.

F. S. HAMMETT

Oligodynamic action of distilled water on metallic copper and its oxides. H. WERNICKE AND A. SORDELLI. *Anales. asoc. quim. Argentina* 9, 145-82 (1921); *Physiol. Abstracts* 6, 407 (1921).—Distd. water becomes oligodynamically active in the presence of Cu or its oxides only when soln. of Cu occurs. This soln. does not take place in an atm. of O_2 or of H_2 , but occurs in the presence of either gas or of air when either CO_2 or free H-ions are present. The oligodynamic action is probably due to adsorption.

JOSEPH S. HEPBURN

Experimental anemia produced by saponin. J. FIRKET. *Compt. rend. soc. belge. biol.* 1921, 727-9; *Physiol. Abstracts* 6, 594(1922).—Saponin produces hyperplasia and not aplasia of the bone marrow; however, it also produces diffuse hemorrhages, and the resulting cicatrices render the functional hyperplasia ineffectual. J. S. H.

Action of saponin upon the platelets and their regeneration. J. FIRKET. *Compt. rend. soc. belge. biol.* 1921, 730-2; *Physiol. Abstracts* 6, 589(1922).—A myeloid metaplasia of the megacaryocyte type appears in the liver and the spleen. The megacaryocytes appear to respond to the most serious injuries to the blood, for the lytic action of saponin is still more energetic on the platelets than on the erythrocytes. J. S. H.

Contribution to the study of the vascular and nerve reactions following the injection of peptone with the aid of a complex dye. J. GAUTRELET. *Compt. rend. soc. biol.* 85, 915-6(1921).—In a normal dog, intravenous injection of nigrosine produces a decrease in blood pressure of long duration; this decrease is intensified by a previous injection of either thionine, which by itself has no effect on the blood pressure, or peptone. However, if peptone be first injected, followed by thionine, then by nigrosine, the fall in blood pressure does not occur. Transfusion of blood from a dog, which has received peptone intravenously, to a normal dog prevents the lowering of the blood pressure of the latter by thionine followed by nigrosine. JOSEPH S. HEPBURN

Behavior of the renal secretory epithelium toward suspensions of finely granular substances introduced into the circulation. F. BERNUCCI. *Il Morgagni* 64, 316-24 (1921); *Physiol. Abstracts* 7, 47-8(1922).—Methylene blue, indigo-carmin, and India ink were suspended in physiol. saline soln.; and the suspensions were injected intravenously into guinea pigs. On normal, healthy animals, the pigments accumulated in the cells lining the convoluted tubules and ascending branch of Henle's loop; they usually collected around the nucleus and the luminal cytoplasm. The cells contg. the pigment granules were larger than normal; their cytoplasm had lost the usual rod-like appearance, and was characterized by dense areas alternating with rarefied areas. In animals suffering from subacute HgCl₂ poisoning, which had affected the kidneys, the power to ingest the pigment granules either decreased or disappeared. JOSEPH S. HEPBURN

Latrodectus mactans and its use. L. J. BOYD. *J. Am. Inst. Homeopathy* 15, 406-9(1922).—A description of the physiol. action of the venom of this spider. JOSEPH S. HEPBURN

Phosphorus—its relationship to diabetes and acidosis. A. G. NASR. *J. Am. Inst. Homeopathy* 15, 718-24(1923).—The clinical symptoms produced by P are identical with those occurring in diabetes which is approaching the coma of acidosis. In both P poisoning and diabetes, the glycogenic function of the liver is affected; craving for sugar, glucosuria, and sugar intolerance occur; the metabolism of fat becomes abnormal, and fat is deposited in the parenchymatous organs. JOSEPH S. HEPBURN

Pernicious and secondary anemias treated with germanium dioxide. J. L. LENKER. *Penn. Med. J.* 26, 86-9(1922).—Subcutaneous administration of GeO₂ as Na germanate is practically painless, is followed by very rapid absorption, and rarely produces any reaction or sore of any extent. It has some value in cases of pernicious anemia of recent standing, and is superior to blood transfusion. Given by mouth in doses of 40 mg., it apparently had no therapeutic value. In secondary anemias GeO₂ certainly cannot be displaced. JOSEPH S. HEPBURN

Action of novocaine on the tonus of skeletal muscle. S. DE BOER. *Proc. Acad. Sci. Amsterdam* 24, 185-6(1922).—See C. A. 16, 3693. JOSEPH S. HEPBURN

Action of quinidine on the heart. F. ARRILLAGA, J. GUGLIEMMETTI, AND C. WALDORF. *Rev. Asoc. Med. Argent. (Soc. Biol.* 2, 124), 34, 454(1921); *Physiol. Abstracts* 6, 525(1921); cf. C. A. 17, 424.—Quinidine exerts a hypotensive action on the dog, and produces cardiac acceleration, then bradycardia; the chronaxia of the heart increases as a

result of decreased excitability; the refractory period increases. In the frog the extra systoles disappear. Auricular fibrillation can no longer be produced in a dog by a faradic current, and is arrested, if it already exists, by an intravenous injection. The vagus loses its excitability in both the dog and the frog, first the preganglionic trunk, later the postganglionic fibers. The accelerators retain their excitability for a long time. Quinidine is antagonistic to the hypertensive action of adrenalin. JOSEPH S. HEPBURN

Contribution to the study of colloidoclasia. P. BRUSSELMANS. *Rev. med. Louvain* 1921, 223-32; *Physiol. Abstracts* 6, 594(1922).—A colloidoclastic crisis, produced by intravenous administration of neoarsphenamine, cured a case of parenchymatous corneitis. Colloidoclastic therapy and its dangers are discussed. JOSEPH S. HEPBURN

Disseminated lesions of the nervous system produced by an unsaturated aliphatic base. R. LUZZATTO AND A. LEVI. *Riforma med.* 37, 1148-9(1921); *Physiol. Abstracts* 7, 59(1922).—Vinylamine-HCl, administered to rabbits subcutaneously, intravenously, or intraperitoneally, in doses ranging from 0.005 g. to 0.008 g. per kg. of body wt., produces disseminated lesions of the white substance of the spinal cord. Intracerebral administration of smaller doses (0.001 g. to 0.003 g. per kg.) produces the same result, which, however, is more widespread after approx. 4 days. JOSEPH S. HEPBURN

The curative and prophylactic action of the acetyl derivative of hydroxylamino-benzenearsonic acid (190 or stovarsol), administered by the digestive tract in syphilis. C. LEVADITI AND L. NAVARRO-MARTIN for the experimental part AND L. FOURNIER, L. GUÉNOT AND A. SCHWARTZ for the clinical part. *Ann. inst. Pasteur* 36, 729-46 (1922).—The Ac deriv. of $H_2N(HO)C_6H_4AsO_3H_2$ administered by mouth in doses of 0.1 g. per kg. between 2 hrs. and 8 days after a massive inoculation prevents the development of spirochetal infection in the monkey and rabbit. It is also active as a prophylactic following sexual contamination in the rabbit. In man a dose of 2 g. by mouth, administered 5 hrs. after a massive inoculation in scarified skin, prevents infection. Treatment of individuals who had repeated sexual intercourse with known syphilitics, in the primary stage of the disease, prevented the development of infection, 4-7 g. being used in the course of 5-8 days after exposure. Oral administration of 190 cured exptl. syphilis in the rabbit, and was of proved value on syphilitic skin and mucous lesions in man, though sometimes weak in action. It may be combined with other treatment. E. R. LONG

Pharmacologic studies of a few derivatives of chaulmoogra oil. M. OHARA. *Japan Med. World* 2, 1(1922); *J. Am. Med. Assoc.* 78, 1667.—These studies have shown that sodium gynocardate and ethyl gynocardate produce central paralysis. The toxic action is more marked with the Na gynocardate. On isolated frog heart the ethyl ester had a slight paralytic action. These substances have inhibitory actions on the isolated rabbits intestine. On rabbit uterus they have a stimulating action and seem to act on the muscles themselves. On the blood vessels they have contracting action. L. W. RIGGS

The hemolytic activity and toxicity of a new saponin, aphrogen, prepared from domestic (German) plants. M. MANDELBAUM. *Chem.-Ztg.* 47, 71(1923).—The hemolytic activity of this commercial prepn. is relatively slight. One cc. of a 1 : 400 diln. injected into a 25-g. mouse is not fatal; a 1 : 200 diln. causes death after 96 hrs. The source of the saponin is not given. GEORGE ERIC SIMPSON

Pharmacological and pharmacodynamical study of strophanthic glucosides; strophanthins and ouabain, according to M. Tiffeneau. "P. F." *J. pharm. chim.* 27, 28-35(1923); see *C. A.* 16, 1810, 1988, 2915. S. WALBOOTT

LEVY, A. GOODMAN: *Chloroform Anaesthesia*. London: Bale. 159 pp. 7s 6d.
SOLLMAN, TORALD: *Manual of Pharmacology and its Applications to Therapeutics and Toxicology*. 2nd Ed. revised. Philadelphia: W. B. Saunders Co. 1066 pp. \$7. Reviewed in *J. Am. Med. Assoc.* 80, 502(1923).

I—ZOOLOGY

R. A. GORTNER

The extractives of *Lumbricus terrestris*. D. ACKERMANN AND F. KUTSCHER. *Z. Biol.* 75, 315-24(1922).—Adenine, lysine, betaine, choline, leucine, tyrosine, succinic and lactic acid were extd. from *Lumbricus terrestris*. An interesting point is the fact that adenine is the chief end-product of the nitrogenous metabolism of these worms. Uric acid, urea, creatine and creatinine were not found. Guanine was present only in traces. Arginine also was present only in small amts. The amts. of betaine and choline were so small as to give the idea that they may have been plant residues in the digestive tract.

F. S. HAMMETT

Calorimetry. II. Production of heat in the ontogenetic development of *Bufo vulgaris*. T. GAYDA. *Arch. fisiol.* 19, 211-42(1921); *Physiol. Abstracts* 6, 578-9; cf. C. A. 17, 1488.—The production of heat (cal. per hr. per g.) is 0.037 cal. in the eggs of *Bufo vulgaris* immediately after fecundation; it gradually increases; it is approx. 0.27 cal. when the tadpole leaves the egg; and attains a max. 0.95 cal. when the tadpole begins to swim. Then heat production gradually decreases to 0.34 cal. at the end of metamorphosis. Increased production of heat is due to formation of segmentation spheres in the developing egg, and to the muscular contractions of the tadpole in swimming. The decrease is due to a decrease in the ratio of body surface and body vol. as growth occurs. The total amt. of heat produced by the developing eggs in 8 days is, on the av., 30 cal. per g. or 0.12 cal. per egg; that produced by the tadpole in 120 days is approx. 1868 cal. per g. or 67 cal. per tadpole. The no. of cal. per g. produced by tadpoles in doubling their body wt. increase with the age of the tadpoles. Heat production by adult toads is approx. the same as that by tadpoles, and lies between 0.29 and 0.51 cal. per hr. per g.; it is greater in males than in females. (V) Production of heat by tadpoles fed thyroid and thymus. T. GAYDA. *Arch. fisiol.* 19, 267-85(1921); *Physiol. Abstracts* 6, 636; cf. C. A. 17, 1484.—Production of heat by tadpoles is greater on a diet of thyroid or thymus than on a diet of meat. Thyroid acts specifically to increase heat production. Thymus increases heat production as a result of increased ingestion of food."

JOSEPH S. HEPBURN

Reason for the existence of the stomach of the gnathostomes. A. LAMEERE. *Bull. soc. sci. med. natur. Bruxelles* 1921, 125-31; *Physiol. Abstracts* 6, 574(1922).—In the vertebrate gnathostomes, the stomach appears as an elongation of the pharynx containing cells for the secretion of pepsin and HCl. The human stomach owes its origin to the mode of alimentation of the first selacians.

JOSEPH S. HEPBURN

Chemical composition of the egg and the tadpole of *Rana temporaria*. FAURE FREMET AND DU VIVIER DE STREEL. *Compt. rend.* 173, 613-6(1921).—The development of the tadpole without an external supply of nutritive material cannot be considered as a simple increase in wt. by imbibition of water, but as a true growth of which the chief characteristic is "autotropism."

JOSEPH S. HEPBURN

Cytological and microchemical study of the celomic erythrocytes of *Terehella lapidaria*. MARC ROMIEU. *Compt. rend.* 173, 786-8(1921).—These erythrocytes have an elastic membrane, a somewhat chromatic nucleus which is frequently found in amitotic division, fatty granules suspended in a liquid medium which is rich in hemoglobin, and excretory granules.

JOSEPH S. HEPBURN

The question of absorption in the protozoa—Overton's membrane. B. SOKOLOFF. *Compt. rend. soc. belg. biol.* 1921, 1101-2; *Physiol. Abstracts* 7, 11(1922).—A semipermeable membrane, which actively absorbs and adsorbs, exists in the protozoa; its existence can be shown physiologically in protozoa in the free state, and morphologically in protozoa in the parasitic state.

JOSEPH S. HEPBURN

p-Dichlorobenzene as a fumigant in the entomological museum. H. H. KNIGHT. *Entomol. News* 34, 57(1923).—*p*-Dichlorobenzene is used to kill *Tribolium confusum* and dermestid larvae in museum collections.
CHAS. H. RICHARDSON

12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

Report on metals in foods. W. F. CLARKE. *J. Assoc. Official Agr. Chem.* 6, 28-31(1922).—The Penniman method for Sn in foods after modification, providing a wet combustion, pptn. of Sn by Zn and Fe and titration of SnCl_2 with 0.01 N I, was recommended for further study after collaborative work (cf. C. A. 16, 1812).

H. A. LEPPER

The absorption of "cyclon" by various foodstuffs. J. D. JANSEN, W. SCHUT AND M. WAGENAAR. *Chem. Weekblad* 19, 373-5(1922).—"Cyclon," a com. liquid disinfectant, is a mixt. of CNCO_2H and CICO_2Et . Its chiefly active product of decompn. in contact with moist air is HCN. After intensive evapn. of "cyclon," the air inside a ship contained 0.5 mg. HCN per l. Various foodstuffs kept in that air contained up to 700 mg. HCN per kg.

R. BEUTNER

The making of vanilla extract. F. N. FOOT. *Spice Mill* 46, 158-60(1923).

C. W. TRIGG

Synthetic sweetening agents. O. BEYER. *Z. angew. Chem.* 35, 271-2(1922).—The methods given for the quant. sepn. of *o*- and *p*-toluenesulfonamide and of saccharin and *p*-sulfaminobenzoic acid by B. in his book *Kontrolle und Herstellung von Saccharin* were never put forward by him as being either reliable or accurate, but only recorded to show on what lines expts. had been made by others.

J. S. C. I.

Report on coffee. H. A. LEPPER. *J. Assoc. Official Agr. Chem.* 6, 106(1922).—The Power and Chesnut method for caffeine in coffee (C. A. 13, 2564) was recommended for official adoption after changing the 10 cc. of 10% H_2SO_4 used for hydrolyzing saponins to 20 cc. (cf. C. A. 16, 1994, 1995).

H. A. LEPPER

Report on tea. R. E. ANDREW. *J. Assoc. Official Agr. Chem.* 6, 107-11(1922).—The collaborative results on the detn. of caffeine in tea by the Power-Chesnut method, the Bailey-Andrew method (previously proposed, C. A. 16, 1994) and the modified Stablschmidt led to the recommendation of the official adoption of the first two.

H. A. LEPPER

The chemistry of tea. VI. Physiological aspect of tannin. C. W. TRIGG. *Tea Coffee Trade J.* 44, 71-2(1923); cf. C. A. 17, 157.—Manuf. of tannin-poor teas is discussed. The action in the alimentary tract of the tannin of clear tea and of that of tea with added milk are briefly treated.

C. W. T.

Report on spices and other condiments. A. E. PAUL. *J. Assoc. Official Agr. Chem.* 6, 92-7(1922).—Four methods for the detn. of crude fiber in prepared mustard were studied by collaborators. The "personal equation" enters into this detn. to a marked degree. The method suggested by Hilts and Hertwig is recommended for tentative adoption. The tentative method for detn. of volatile oil in mustard seed is recommended for official adoption after study.

H. A. LEPPER

Homogenizer an improvement. A. W. LANDSTROM. *Baking Tech.* 1, No. 12, 350-7(1922).—Under the conditions studied in baking the expts. tend to establish the fact that homogenization is an improvement over ordinary methods. Better absorption, vol., color of crumb, a better grain and a better texture are noticeable.

RUTH BUCHANAN

Homogenizer reduces losses. A. W. LANDSTROM. *Baking Tech.* 2, No. 1, 22-4(1923).—Under the outlined conditions of the expts. homogenization of ingredients seems to reduce wt. losses of bread on storage.

RUTH BUCHANAN

Variations in the Concord grape during ripening. H. A. NOYES, H. T. KING AND J. H. MARTSOLF. *J. Assoc. Official Agr. Chem.* 6, 197-205(1922).—Results reported on grape juices, sampled from regular factory production in 1919, show that there is no systematic change in the compn. of grape juice pressed at diff. times during a regular pressing season of 20 days. The general tendency is for sugars to increase and for acids to decrease when grapes are left on the vines. Results on the 1920 crop show that there was no great variation in the wt. of the berry as ripening advanced. Decrease of H_2O content of grapes was noticed as the season advanced but it was not directly proportional to the increase in sugar. After ripening had reached a certain point the changes in sugar were irregular. Hot- and cold-pressed juices showed increases in sugar and decreases in acid as ripening continued while tannin and coloring matter were irregular in both but ran much higher in the hot-press. Results of diff. magnitude were obtained on 1921 grapes but the general 1920 conclusions were unchanged. The great variation in the compn. of ripening Concord grapes cannot be correlated with season and date of harvesting.

H. A. LEPPER

Total non-protein nitrogen content of the hen egg. J. S. HEPBURN. *J. Am. Inst. Homeopathy* 15, 409-12(1922).—The protein-free filtrate, obtained by diln. of white, yolk, or whole egg with water and treatment with 10% Na_2WO_4 soln. and $\frac{1}{2}$ N H_2SO_4 , may be used for the detn. of total non-protein N by the Kjeldahl method. From detns. made on 36 samples from various sources, the conclusion is drawn that the total non-protein N of white, yolk, and whole egg may vary within wide limits, and may not be taken as the sole criterion of edibility; some edible eggs showed a high-value for total non-protein N, some inedible eggs a low value for that constituent. Several percents of the total N of fresh eggs may be present in the non-protein form.

JOSEPH S. HEPBURN

Report on eggs and egg products. H. I. LOURIE. *J. Assoc. Official Agr. Chem.* 6, 4-14(1922).—Methods proposed for the analysis of frozen and liquid egg products include sampling, solids, H_2O ext., acidity of fat, ammonia N, reducing sugars, and indole and skatole; of dried eggs include physical characteristics and zinc; of egg products (egg noodles) include H_2O , ash, NaCl, fat, lecithin P_2O_5 , gasoline color value, and artificial color. No analytical results are reported (cf. C. A. 16, 1812). H. A. LEPPER

Milk and ice cream as fatty foods. JEROME ALEXANDER. *Ind. Eng. Chem.* 15, 254(1923).—Information is set forth which makes it obvious that efficient colloidal protection is of prime importance in insuring the proper digestion of milk and ice cream, particularly the latter.

E. J. C.

Easy and rapid method of preparing protein milk. E. H. BARTLEY. *Arch. Pediatrics* 39, 741-2(1922).—One pint of buttermilk is mixed with an equal vol. of boiling water. The curd which seps. is permitted to settle for 5 to 10 min. The supernatant liquid is decanted. The curd is washed twice with warm water by decantation, then drained free from water, and mixed with a pint of skimmed milk by vigorous stirring with an egg beater. About 20 ounces of a product of the following approx. compn. are obtained: protein 5, sugar 2.8, fat < 1, salts < 0.5%. If the curd from 1 quart of buttermilk be prepd. as directed and then mixed with 1 pint of skim milk plus sufficient water to give a total vol. of 1 quart, the product contains approx. protein 4.6, sugar 2.4, fat 0.5, and salts 0.35%. The product is free from insol. curds, remain in suspension on standing, and may be used instead of albumin milk.

J. S. H.

The heat coagulation of milk. H. H. SOMMER AND E. B. HART. *J. Dairy Sci.* 5, 525-43(1923).—The conclusion reached in a previous article (C. A. 14, 985) was confirmed by the study of a large no. of samples of fresh milk from different cows. Expts. were also made on evapd. milk under com. conditions. The effect of adding small amts. of $Na_3C_6H_5O_7 \cdot 5\frac{1}{2}H_2O$, K_2HPO_4 , $Ca(C_2H_3O_2)_2 \cdot H_2O$ and $NaHCO_3$ was studied.

The effect of these salts on evapd. milk was found to be the same as that on fresh milk. In the manuf. of evapd. milk the salt balance was found to be of importance in order to avoid low sterilization. In a no. of cases the troublesome coagulation of evapd. milk was remedied on a com. scale by the addn. of the proper amt. of $\text{Na}_2\text{C}_2\text{H}_3\text{O}_7 \cdot 5\frac{1}{2}\text{H}_2\text{O}$ or K_2HPO_4 . The milk salts affect the coagulation of milk directly, and not indirectly through change in reaction. If sol. Ca salts are properly balanced with phosphates and citrates the casein is held in soln. even in an acid medium while in the absence of citrates and phosphates the casein is pptd. even though the soln. is alk. O. L. EVENSON

A method for the quantitative determination of gelatin in ice cream. I. W. FERRIS. *J. Dairy Sci.* 5, 555-64(1922).—The amt. of gelatin in ice cream is detd. approx. by removing the casein and fat according to the A.O.A.C. method for the qual. detn. of gelatin in milk and comparing the turbidity produced in the filtrate by picric acid, with a standard by means of a nephelometer. More accurate results are obtained by pptg. the casein and fat with AcOH , sepg. the gelatin with alc., redissolving in hot H_2O and calcg. the % gelatin from $(\alpha)_D^{25}$. The % gelatin in the sample = $(R \times 0.345 \times V \times 100)/(W \times 2 \times (\alpha)_D^{25})$, in which W = wt. of sample, V = vol. of AcOH serum and R = polariscope reading in Ventske degs. in a 2-dm. tube. The % gelatin is also obtained from the N content. The mutarotation was also measured to show the jelly strength of the gelatin used. Results are shown on 21 samples of exptl. ice cream mixes contg. from 0.2 to 1% of gelatin, gelatin of good, medium and poor quality being used.

O. L. EVENSON

Critical study of the value of the simplified molecular constant (S. M. C.) of milk. CH. PORCHER. *Ann. fals.* 16, 16-47(1923).—A very detailed study of the meaning and value of Mathieu and Ferré's S. M. C. (lactose + $11.9 \times \text{Cl}$ (as NaCl), expressed in g. per l. and corrected for the vol. of casein and of fat). From an investigation into the distribution of saline substances and mineral elements in milk, P. and Chevallier (C. A. 15, 3340) conclude that of the difference in f. p. between milk and water (0.552°), 0.111° is due to chlorides (KCl and NaCl) and 0.293° to hydrated lactose; so that the S. M. C. is really a measure, in terms of lactose, of elements which are responsible for 75% of the depression of the f. p., which is the most const. characteristic of milk. It is valuable for detecting watering of milk, and especially for distinguishing between watered milks and naturally weak milks (including pathological milks). It fails in cases where NaCl is added to milk after watering or where milk is watered by means of its own serum. P. also discusses other so-called const. (Bouin, Fouzes-Diacon, solids not fat, Cornalba, Koestler, Kopatschek), showing they are not based on any solid physiol. basis, and that they fail in the crucial cases, i. e., with abnormal milks.

A. P. C.

The seasonal variations of the percent of fat in cow milk. A. C. RAGSDALE AND C. W. TURNER. *J. Dairy Sci.* 5, 544-53(1922).—Data are presented showing the seasonal variations of the % of fat in cow milk, derived from a study of 3763 Guernsey, 299 Jersey, and 95 Holstein-Friesian yearly records. The % of fat in milk, when plotted, follows a general curve, being lowest during summer, then gradually increasing, reaching a peak during the winter months, then again declining. Changes of temp. which accompany different seasons have greater influence upon the % of fat than the advance of lactation. In general no matter when the lactation period begins there is a tendency for the % of fat to rise during the winter months. Cf. C. A. 16, 1816. O. L. EVENSON

Report on cereal foods. C. H. BAILLY. *J. Assoc. Official Agr. Chem.* 6, 60-3 (1922).—Two methods, details of which are given, for detn. of fat in baked cereal products, were studied by collaborators. The results justified the adoption as tentative of the method proposed by C. R. Smith. Add 10 cc. alc., 2 cc. concd. NH_4OH and 3 cc. H_2O to 5 g. of ground sample in a 200-cc. flask. Boil 2 min. on the steam bath,

cool, ext. with 3 25-cc. portions of Et_2O , kneading with glass rod. Decant the Et_2O into a 250-cc. beaker, draining the last as completely as possible. Add another 15-cc. portion of ammoniacal alc. soln. to the extd. material, disintegrate with a glass rod. Repeat the boiling and extn. Evap. the combined Et_2O exts. to dryness and ext. the residue 5 or 6 times with a mixt. of petr. ether and Et_2O (15 cc. of each). Collect the exts. in a dish (do not filter), evap., dry at 100° and weigh. H. A. LEPPER

Studies on wheat flour grades. III. Effect of chlorine bleaching upon the electrolytic resistance and hydrogen-ion concentration of water extracts. C. H. BAILEY AND ARNOLO JOHNSON. *J. Assoc. Official Agr. Chem.* 6, 63-8(1922).—A patent and a clear flour with 0.43 and 0.84% ash, resp., were studied. Lah. bleaching with 20 cc. Cl per 100 g. increased the sp. elec. cond. of the H_2O ext. of the patent 0.48 and of the clear 0.73 ($K_{30} \times 10^4$). On the patent this is equiv. to 0.045% of ash when unbleached flours of varying ash content are compared. Same treatment changed the p_{H} value of the patent 0.34 while the clear changed only 0.17 because of its higher buffer action. Com. bleached samples gave similar results. Bleaching with Cl effects an increase in the buffer action of H_2O exts. of flour. Sp. elec. cond., H-ion concn. and buffer action of flour exts. are increased in direct ratio to the quantity of Cl used. The differences did not disappear on storing 2 months in Mason jars. Methods previously given (*C. A.* 14, 3729) were used. H. A. LEPPER

Gluten as a factor in grading wheat. G. L. TELLER. *Modern Miller* 50, No. 10, 22-3(1923).—Proteins in flour and wheat, the variation of gluten in flour, the N in wheat proteins, the gluten in shriveled wheat, the gluten variation in wheat and flour, the protein in bran, H_2O absorption and gluten and the value of gluten in wheat flour are discussed. RUTH BUCHANAN

Microscopic method for the quantitative determination of rice hulls in rice bran. B. H. SILBERBERG. *J. Assoc. Official Agr. Chem.* 6, 71-2(1922).—Results on official samples of the U. S. Bur. Chemistry by the microscopic method (*C. A.* 16, 597) for rice hulls in rice bran uphold the previous conclusion. It is recommended that the method be retained for tentative adoption. H. A. LEPPER

The reddish coloration of polished rice. KENMARU AOI. *Rept. Imp. Cent. Agr. Expt. Sta., Tokyo* 45, 29-69(1921); *Japan. J. Botany* 1, Abstracts 1(1922).—The color is due to a species of *Oospora*. No coloring matter can be dissolved from infected rice by H_2O , EtOH , Et_2O , C_6H_6 , benzine and other common solvents. In alkalies the color changes from purplish red to reddish purple; acids restore the original color. Nascent H destroys the color. E. J. C.

Report on the determination of shell in cacao products. B. H. SILBERBERG. *J. Assoc. Official Agr. Chem.* 6, 98-101(1922).—Collaborative results justified the recommendation of the adoption as tentative of a microscopic method for the detn. of cacao shell in cacao products. The method is given with a discussion of manipulation (cf. *C. A.* 16, 1819). H. A. LEPPER

Separation of the meat proteins. C. R. MOULTON. *J. Assoc. Official Agr. Chem.* 6, 76-85(1922).—The methods for the sepn. of meat proteins are amplified to allow the approx. subdivision of the N of meat sol. in cold H_2O into globulin (g), albumin (a), proteose (p), peptone and peptide, and amino acid and extractive N. Coagulation of g is made with half-satd. ZnSO_4 . This at $1/2$ satn. coagulates more N as g than does NaCl at satn. Dilg. the ext. reduces the N coagulated. g and a N are readily coagulated by beat in the presence of moist freshly pptd. MgCO_3 . The difference between this and g is taken as a . The filtrates and washings from heat coagulation are satd. with ZnSO_4 and acidified to ppt. p . A larger quantity of acid increased the p N obtained. g , a and p are coagulated by satd. ZnSO_4 when sufficiently acidified with H_2SO_4 . A graph is given from which the required amt. of acid can be estd. Dilm. of the ext. from a previous

removal of *g* gives a smaller recovery in this fraction by an amt. considerably greater than the *g* removed. Difficulty was experienced in detg. the amino acid extractive N by coagulating the other fractions with tannic acid and NaCl. Fractions designated by specific names are not claimed to be pure. Recommendations for further work are made.

H. A. LEPPER

The preservation of food by freezing with special reference to fish and meat. WALTER STILES. Dept. Sci. Ind. Research Food Investigation Board, *Sp. Rept.* No. 7, 186 pp. (1922); cf. *C. A.* 15, 3338.—A presentation of the scientific principles involved in the preservation of food in the frozen condition, the major topics of which are the physics and chemistry of the freezing process, the diff. freezing methods, the storage of food substances in the frozen condition, thawing, and the preservation of fish and meat by freezing.

H. A. LEPPER

The preservation of fish in ice. L. H. ALMV, F. FIELD AND H. R. HILL. *Am. Food J.* 18, No. 1, 36-8 (1923).—The wt. of the fish first increased then decreased, a net loss occurring in fish on bottom layers. A loss of mineral and org. constituents during the longer storage periods was indicated, particularly in gutted fish. No change in present practice of gutting most species is recommended from the results.

H. A. LEPPER

The molds of frozen meat. BIDAULT. *Rev. gen. froid* 3, 216 (1922); *Bul. mens. office internat. d'hyg. publ.* 14, 1579.—A general paper giving details of technique of identification, notes on the frequency of various species, and preventive measures. Cf. *C. A.* 16, 2370.

JACK J. HINMAN, JR.

Amino acids in the globulin and albumin fraction of beef flesh. C. R. MOULTON. *J. Assoc. Official Agr. Chem.* 6, 86-90 (1922).—The amino acid N distribution of 3 samples of H₂O-sol., heat-coagulable proteins from lean round of beef is reported with details of methods used. They are in general those devised by Van Slyke.

H. A. LEPPER

A preliminary study of the digestive secretions of pickerel and perch. CAROLINE WALKER MUNRO. *Trans. Wisconsin Acad. Sci.* 20, 269-73 (1921).—Glycerol exts. of the mucosa of stomach and of intestine, as well as an ext. of the pancreas, showed considerable proteolytic activity on egg white in the case of the pickerel. However, the pickerel apparently has no enzyme for the inversion of sugars. The perch has no pancreas but both stomach and intestine were found to contain a proteolytic enzyme. The intestinal ext. of the perch was capable of inverting cane sugar. These findings are correlated with the food habits of the fish studied.

A. L. BARKER

Sliced smoked salmon. P. BUTTENBERG. *Chem.-Ztg.* 47, 6 (1923).—In Germany, salted salmon of domestic or imported origin (American) is soaked, smoked in the cold, sliced, steeped in salad oil and so sold or tinned. Fish of the cod family is similarly treated, colored with dyes and satd. with oil to give the color and fat content in imitation of salmon. Distinguishing characteristics based on physical appearance and chem. examn. are given. Ext. the sample with boiling petr. ether and filter. Salmon gives an orange-red filtrate leaving an orange-red oil on evapn. with refractometer reading of 60-62.5 at 40° while substitute gives a colorless filtrate, light yellow oil with refractometer reading of 55-57. Boil the residue after extn. with H₂O and alc. mixt. (1 : 1) and filter. Salmon yields a colorless filtrate while substitute gives an intense orange filtrate which remains on boiling with HgO and dyes wool in boiling AcOH.

H. A. LEPPER

Lard substitute (hydrogenated oil). C. ELLIS. U. S. 1,416,004, Feb. 20. A mixt. of coconut oil 85-90 and peanut oil or Brazil-nut oil 10-15% is treated with H at a temp. of 160-180° with a catalyst formed from Ni formate and oil and after the

hydrogenation is about 80% complete the catalyst is removed by filtration and the hydrogenation is continued with Pd as the catalyst and at a somewhat lower temp. until the I no. is reduced to approx. zero. The resulting product is adapted for use as a lard substitute in foods. It may be deodorized by treatment with steam and may also be aerated and chilled to give it a white appearance resembling lard. Other oils also may be used as starting materials.

Drying fruits or other materials at low temperatures. F. MAUS. U. S. 1,446,054, Feb. 20. Prunes, nuts, apricots or other material to be dried at relatively low temps. are treated countercurrentwise with air which is cooler and drier than the material being treated. A portion of the air, heated from contact with the material, is used to raise the temp. of highly refrigerated dried air before it is brought into contact with the material, so that the temp. and moisture content of the material may be progressively reduced at a regulated speed.

Evaporator for fruit and vegetable pulps. F. C. MARZO. U. S. 1,446,651, Feb. 27. The material being evapd. is passed continuously through a steam-jacketed horizontal evapg. drum.

Apparatus for drying fish, fruit, vegetables or other substances. W. H. PERRY. U. S. 1,446,580, Feb. 27. The material to be dried is carried on a foraminous belt conveyor through a drying chamber while a current of drying gas, *e. g.*, warm air, is passed over it.

13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

Industrial filtration. LÉONCE FABRE. *Giorn. chim. ind. applicata* 4, 528-32 (1922).—Monograph, describing especially the Moore Zenith filter, with 2 photographs and diagrams. ROBERT S. POSMONTIER

Atmosphere pollution by industrial wastes. R. E. SWAIN. *Ind. Eng. Chem.* 15, 206-301 (1923).—In this 6th lecture under the Chandler Foundation, S. gives a very complete account of the cause and prevention of damage to crops by smelter fumes contg. SO₂. E. G. R. ARDACH

Two fatalities due to inhaling phosgene. SHERIDAN DELÉPINE. *J. Ind. Hyg.* 4, 433-40 (1923).—Two cases of exposure to COCl₂ with death resulting in 19 and 22 hours are cited. COCl₂ is a powerful irritant to air passages; it sets up profuse exudation which mixed with desquamated cells from the walls of the air passages finally causes their obstruction. The condition is further aggravated by a contraction of the bronchial muscles due to the irritation. A treatment is suggested which includes the reduction of the exudation by the injection of sugar solns. and the reduction of spasm by the use of an anodyne. A. A. CHRISTMAN

Observations on the effects of exposure to arsenic chloride upon health. SHERIDAN DELÉPINE. *J. Ind. Hyg.* 4, 410-23 (1923); cf. *C. A.* 17, 1074.—When AsCl₃ is exposed to moist or dry air gases rich in As are emitted. If the air is fairly dry these gases are invisible but if the air is moist, visible fumes of AsOCl and allied products are formed and settle out on solid objects. Examn. of hair and urine of workmen employed in the manuf. of AsCl₃ showed the presence of appreciable amts. of As. Poisoning by AsCl₃ may be avoided by putting a water seal at any point in the manuf. app. where the AsCl₃ may escape. A. A. CHRISTMAN

Comparative investigations of the toxicity of some samples of benzene and particularly of solutions of rubber in benzene for use on fabrics. ANGELO PUGLIESE. *Rend. ist. Lombardo* 55, 404-8 (1922).—The toxicity of pure and impure C₆H₆ and of rubber-C₆H₆ solns. was studied by means of animals. Three procedures were used:

(1) inhalation with masks; (2) respiration of C_6H_6 vapor in closed chambers and (3) respiration of vapor dild. with air by open windows. Dogs were used in (1) and dogs, rabbits, guinea pigs, white mice and pigeons in (2) and (3). Chem. pure C_6H_6 had the most rapid and intense toxic action. The toxic effect of impure C_6H_6 used in the rubber industry was relatively low. A sample of C_6H_6 having the most obnoxious odor was the least toxic. After 1 mo. this became intense yellow with a ppt. and the toxicity increased. Rubber solns. were spread on cloth and the animals exposed to the vapor under the same conditions as before. By this procedure the toxic effect was not acute insofar as respiration was normal, but the body temp. decreased, with a max. decrease for pure C_6H_6 solns. of rubber. In contrast to the other animals, the pigeons showed no decrease in temp., but additional prolonged treatment with C_6H_6 caused a decrease, with various symptoms of chronic poisoning. Some animals developed, by repeated action of C_6H_6 , a hypersensitivity and were poisoned by amts. which originally were easily tolerated. This conforms to the frequent belated symptoms of poisoning in rubber workers exposed to C_6H_6 . Greatly increased thirst was a prominent symptom in all animals, particularly in rabbits and guinea pigs. A considerable decrease in white corpuscles occurred, but the no. became normal some time after removal from C_6H_6 . With dildn. by fresh air, the animals were not poisoned even by much higher concns. than the max. possible without aeration. By allowing a min. space for each operator and with sufficient ventilation, C_6H_6 poisoning in factories should be easily avoided. Conditions at the Pirelli works are deemed satisfactory, where each worker has 58.5 m.³ with replacement of 60 m.³ of air per min. CaI_2 should not be touched by hand for absorption is considerable. It is recommended that periodical examn. of the blood for its leucocyte count be made to detect incipient cases of poisoning.

C. C. DAVIS

Experimental investigations of the toxic action of benzene, petroleum ether and toluene. ANGELO PUOLIGNESE. *Rend. ist. Lombardo* 55, 443-4(1922).—Expts. similar to those with C_6H_6 (cf. preceding abstract) are reported for benzene of d. 0.74 (A) (Rumanian) and 0.71 (B), for petr. ether (C) and for com. PhMe (D) and pure PhMe (E). D, E, A, B and C were definitely toxic, increasing in the order given, but all less than C_6H_6 . Aeration expts. were, therefore, not attempted because high concns. of C_6H_6 were necessary to obtain definite poisoning under such conditions. Acute intoxication, ending in convulsions, was observed with C and B. As with C_6H_6 , repeated treatment with A and B caused a hypersensitivity. Though D and E were less toxic than A and B, their vapors irritated to a much greater degree the mucous membranes and conjunctiva, causing lachrymation, sneezing, and coughing. The substitution of C_6H_6 in rubber factories by A or B is imprudent, for though less toxic than C_6H_6 , A and B give rise to slow cumulative poisoning. To prevent industrial poisoning, precautions similar to those for C_6H_6 must be taken.

C. C. DAVIS

Pennsylvania lubricating oils as against others. ANON. *Nat. Petroleum News* 15, No. 7, 51-3(1923).—Answers to questionnaires sent out by the Nat. Petr. News to 216 jobbers show a general preference for Penn. lubricating oils because of their paraffin content. It is stated that other oils, however, have been found to give equally good results.

D. F. BROWN

The preparation, properties and testing of petroleum lubricants. RICHARD KISSLING. *Chem.-Ztg.* 47, 77-80, 100-2(1923).—A brief description of present-day processes and methods.

W. F. FARAGHER

Lubrication. H. MOORE. *Oil Eng. & Finance* 3, 232(1923).—A comparison of lubricating oils from various sources shows sp. gr. and viscosity at 70, 100 and 200° F., resp., for Russian oils 0.911, 1230, 390, 53; for Pennsylvanian 0.898, 1230, 415, 58; for Texas 0.935, 1390, 385, 49. The Russian oil of to-day is about the same or slightly

inferior to the pre-war quality. It has, however, been largely supplanted by the asphalt oils known as zero cold test oils. D. F. BROWN

The deleterious effect of fibers on insulating varnish. W. OGAWA. *Denkinotomo (Electricians' Friend)*, Tokyo No. 562, 297-8(1923).—The deleterious effect of fibers on the insulating power of transformer oil was brought to light by Hirobe, Ogawa and Kubo (*C. A.* 11, 317). A similar conclusion as to the effect of fibers in insulating varnish was made by O. Dielec. strength of a varnish film contaminated with a very small amt. of fibers was easily brought down to $1/2$ or less in comparison with the pure film free from fiber. O. points out the importance of cleanliness in varnish making, and also suggests some useful points in the manuf. of insulating oil-paper and empire cloth. Further expts. are under way. W. OGAWA

Carbon dioxide versus ammonia as a refrigerant. H. T. MACINTIRE. *Power* 57, 288-90(1923).—CO₂ requires more power and more cooling water per ton and higher operating pressure than NH₃. Since it is the best safety refrigerant known its use is increasing. Characteristics of CO₂ and NH₃ are compared in charts. D. B. DILL

Accelerated reactions in pulsating gaseous currents. W. B. VAN ARSDEL. *Chem. Met. Eng.* 28, 242(1923).—Pulsating gas currents give high reading on metering devices, probably through absorption of some of the energy of the pulsations. Perhaps the same phenomenon would cause an acceleration of reactions in a pulsating gas stream. (Cf. Deschamps and Shadgen, *C. A.* 17, 1094.) F. C. Z.

Accelerated reactions in pulsating gaseous currents. F. C. ZEISBERG. *Chem. Met. Eng.* 28, 242(1923).—Improvements in absorption resulting from impressing pulsations on the gas current are probably more easily explicable from the standpoint of better liquid distribution than from better gas distribution. (Cf. Deschamps and Shadgen, *C. A.* 17, 1094.) F. C. Z.

Pharmacology of some phenylenediamines (HANZLIK) 11H.

GUÉRIN, MAURICE: Les brevets d'invention dans l'industrie chimique. Paris: Libr. Dalloz. Fr. 12.

HEMMING, EMILE: *Plastics and Molded Electrical Insulation*. New York: The Chemical Catalog Co., Inc. 313 pp. \$5.

STILLMAN, ALBERT L.: *Briquetting*. Easton, Pa.: Chemical Publishing Co. 466 pp. \$6.00.

Selenium oxychloride as a solvent of carbon compounds. V. LENHER. U. S. 1,445,329, Feb. 13. SeOCl₂ is used to dissolve coatings of paint or varnish, rubber resins, glue or other organic substances.

Emulsifying liquids of different densities. E. E. WERNER. U. S. 1,445,427, Feb. 13. Emulsions of liquids of different d., e. g., cottonseed oil and milk or oil and aq. gum arabic soln., are formed by directing a stream of the liquids on to the smooth face of a rotating disk so as to disperse the lighter liquid within the heavier.

Measuring the flow of gas. C. W. HINMAN. U. S. 1,446,461, Feb. 27. Heat is abstracted from flowing illuminating gas or other gas by means of a current of H₂O and constant temp. differences are maintained between the temps. of the H₂O before and after it is acted upon by the gas. The flow of gas is detd. by calcn. based on heat absorption.

Stabilizing electric resistance materials. F. R. PARKER. U. S. 1,446,720, Feb. 27. Materials such as carbonaceous or aggregated comminuted substances having unstable resistance are stabilized by passing through them an elec. current greater than that to be carried by them in service.

Revivifying spent catalysts. T. MINGLEY, JR. U. S. 1,446,984, Feb. 27. Spent oxide catalytic material, e. g., Ni oxide from hydrogenation, is revived by treatment with NO_2 and H_2O and heating.

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW AND G. C. BAKER

New method of gaging the discharge of rivers. J. JOLY. *Sci. Proc. Roy. Dublin Soc.* 16, 489-91(1922); *Science Abstracts* 25B, 376.—The ordinary chem. process is modified by substituting a radioactive method. A very dil. soln. of known strength of a radioactive substance (say pitchblende) is introduced into the river, and the Ra content of the water at any known point detd. by well known radioactive methods (emanation, electroscope, or other). This new method permits of very great accuracy, even when extremely dil. pitchblende solns. (of almost negligible cost—say a few s.) are used.

H. G.

Inspection of water supplies. F. DIENERT. *Tech. sanit. munic.* 1922, 188-193; *Water & Water Eng.* 24, 459(1923).—The underground sources are especially considered; and the need of studying geological formations, rates of flow of water through them, and of applying this knowledge to the inspection of the supplies are urged. Frequent detns. of temp. of water indicate possible origin and rate of circulation. Supplies from wooded areas are always colder than those from cultivated ground devoid of trees.

JACK J. HINMAN, JR.

Water supply dangers from sanitary standpoint. E. S. CHASE. *Can. Eng.* 44, 163-6(1923).—The hazards to surface and ground water supplies, and to water in distribution systems are reviewed.

LANGDON PEARSE

The water supply of Philadelphia. ANON. *Bureau of Munic. Research of Philadelphia* 1922, 1-53; *Pub. Health Eng. Abstracts* Mar. 10, 1923.—Shortcomings of the present supply are (a) inadequate pressure and vol. in certain districts, (b) break-downs in plant and equipment followed by interruptions to the supply, (c) occasional tastes and odors largely derived from the Schuylkill supplies due to decaying org. matter and industrial wastes, chiefly from coal-tar products, and (d) occasional bacteriol contamination. Recommendations include abandoning Schuylkill supplies and possibly that derived from the Delaware River. Proposed future sources are Perkiomen, Neshamings and Tohickon streams impounded, with possible future extension to the Lehigh and Delaware tributaries.

G. C. BAKER

Shallow wells as source of municipal supply. E. J. WATERMAN. *Eng. Contr.* 58, 128-31(1922).—The principles of location and construction are discussed, examples being cited. Surface pollution as well as town drainage must be avoided.

L. P.

Installation for the removal of iron from the drinking water for the city of Griefswald. KROFF. *Die Wasserkraft* 1922, 334-5; *Water & Water Eng.* 24, 457.—App. and innovations for reducing clogging and difficulty of cleaning are detailed. Water flows through sprinklers in the form of pipe bundles, each pipe of which delivers water into a metal saucer from the edges of which it falls as a spray.

J. J. HINMAN, JR.

Hydrogen-ion concentration and water purification. F. C. MORTENSEN. *Eng. Contr.* 58, 160-2(1922).—Trials at Cedar Rapids of the p_{H} method of control, on a river water having an av. p_{H} of 7.0 and after alum treatment 6.6 to 6.8 and after filtration 7.0, are described. Cl works best at p_{H} 7.0 or lower. When hardness drops below 100 p. p. m. some lime is added to the filtered water.

LANGDON PEARSE

An experimental study of the relation of hydrogen-ion concentrations to the formation of floc in alum solutions. E. J. THERIAULT AND W. M. CLARK. *Public Health Repts.* 38, 181-98(1923).—The p_{H} of the final mixt. of water and alum is of fundamental

importance in the formation of floc. When other possible factors were left out of consideration, optimum conditions for floc formation in dil. solns. were found at pH about 5.5. The more dil. the water in total salt content, and the less alum added, the narrower the pH zone with optimum floc formation was found. In exptl. studies the time of floc formation was largely dependent upon the vols. of solns. worked with and whether they were agitated. Control of pH should permit economy in alum dosage. Theoretical considerations are an important part of the paper. G. C. BAKER

Economical control of chemical dosage in filter plants. R. A. MADDOCK. *Public Works* 53, 258-60; *Munic. County Eng.* 63, 238-40(1922).—Overdosage of 25% to dose 75% untreated water for coagulation, formation of a mat of $Al(OH)_3$ on the surface of the filter bed, and chlorination before or after filtration are discussed. All Cl app. should be in duplicate. LANGDON PEARSE

Taste and odor in chlorinated water. EDWARD BARTOW AND R. M. WARREN. *Eng. Contr.* 54, 148-9(1922); *Can. Eng.* 44, 621-2(1922).—See C. A. 17, 842. L. P.

Chlorination of water. ALEXANDER HOUSTON. *Can. Eng.* 44, 154-5(1923).—The use of Cl on the London water supply has been very successful; in some cases Cl has been followed by $KMnO_4$ or SO_2 . Cl was 1 in 2.5-4.0 mil. imp. gal. L. P.

The chlorination of water. ALEX. HOUSTON. *Engineer* 134, 198(1922); cf. preceding abstract.—An abstract of the 16th annual report on the "Results of the chem. and bacteriol. examn. of the London waters." Ninety % of the total London water supply during the past year (1921) has been chlorinated. No complaints on account of taste were received. Chlorination "succeeds considerably better than storage on the av. and is nearly 7 times superior during the winter months." D. B. DILL

Cost of filtering and pumping water at Providence, R. I. M. H. BRONSDEN. *Ann. Report* 1921, *Eng. Contr.* 59, 124(1923). LANGDON PEARSE

Importance of filter sand and gravel in filtration plants. A. O. TRUE. *Eng. Contr.* 59, 121-3(1923).—Mud balls, conditions during wash, voids in sand, and construction are discussed. An effective size of 0.35 to 0.45 mm. and uniform coeff. of 1.6, with 20 in between sand and lip of wash water trough, are recommended. 18 in. gravel will hold down the wash water to a rate of 15 gal. per sq. ft. per min. LANGDON PEARSE

Laboratory control of filtration. G. D. NORCORM. *N. C. Sect. Am. Water Works; Eng. Contr.* 59, 114-6(1923).—Detns. of alk. and pH for optimum coagulation ($pH = 4.2$) are given. Actual results show pH of 6.0 in the filtered water. A secondary dose of lime is added near the end of a 10 hr. sedimentation. LANGDON PEARSE

Operation of mechanical filters and value of simple tests. P. G. TURNER. *Eng. Contr.* 58, 145-7(1922).—Determinations of alk., turbidity, free alum, free Cl, tastes, odors and tests for dosage of chemicals are recommended. Details of operation are described. LANGDON PEARSE

The use of filter rewash. J. H. SUGGS. *Public Works* 54, 22-3(1923).—The rewash if improperly used does more harm than good. LANGDON PEARSE

A simple and practical method for the bacteriological analysis of water. A. VERDA. *Schweiz. Apoth. Ztg.* 60, 651-4, 671-6(1922).—The method detcs. the no. of microbes that form colonies on a surface of gelatin, agar or other *solid* medium, by leaving the H_2O in contact with it for several min. This is done by means of Esmarch tubes coated with the culture medium; they are filled with the H_2O to a mark and after 10 min. the H_2O is gently poured off; for cold H_2O the time of contact may be longer. The tubes are closed with cotton and the mouths sterilized by a flame and placed in a thermostat for 2-3 days at 37° (agar-agar), 30° (gelatin-agar), or 22-25° (gelatin); finally the colonies are counted. By comparison with standard methods, V. finds that 10 times the no. of colonies on 30 cm.² area gives approx. the no. of bacteria per cc. The tubes being

portable, inoculation may take place at the source of the H_2O . The method may also be used for the detn. of the relative no. of bacteria in milk. S. WALDBOTT

A new practical reagent for detecting nitrites in water. G. RODILLON. *J. pharm. chim.* 26, 376-9(1922); 27, 64-5(1923).—The reagent, a soln. of white resorcinol (3 g.) in pure H_2SO_4 (50 g.), produces a rose-red zone when placed underneath H_2O contg. nitrites. The priority of Denigès in the use of such a soln. is noted. S. W.

Sterilization and filtration of water by the "ferrochlore" process. NOËL ADAM. *Rev. hyg.* 12, 1169-75(1922).—The process is based upon the use of $Ca(OCl)_2$ and either $FeCl_3$ or iron-bearing $Al_2(SO_4)_3$. In expts. reported 0.75 to 4.0 p. p. m. $Ca(OCl)_2$, and 10-20 p. p. m. $FeCl_3$ or 30-40 p. p. m. alum were used. JACK J. HINMAN, JR.

The Hottingher method of water sterilization. GUIDO RIGOBELLO. *L'Igiene moderna* 15, 166(1922); *Bull. mens. office internat. d'hyg. pub.* 14, 1575(1922).—Silver is fixed by means of a colloidal soln. on the interior of porous earthenware jars, or alcazazas. It has been claimed that water will be safe for drinking after one hr. in the jar. The method has been approved by the health authorities of Brazil. Expt. showed that the action is limited and not capable of guaranteeing freedom from all infection, but it is of some value from simplicity and economy for use in remote places.

JACK J. HINMAN, JR.

Germicidal effect of acid mine drainage. W. L. STEVENSON. *Public Works* 53, 264-5(1922).—An investigation of the Lackawanna and Susquehanna Rivers shows that acid mine drainage reduces the bacterial content more than 99% and prevents offensive decompn. of sewage reaching the rivers. Both lab. and field investigations are described. LANGDON PEARSE

Bio-aeration method of sewage treatment. JOHN HAWORTH AND F. W. HODGKINSON. *Inst. Munic. County Eng.* 1922; *Can. Eng.* 44, 103-7(1923).—Mechanical agitation of activated sludge by the use of paddle wheels is described. The plant consists of an aeration tank with 18 channels 4 ft. wide by 4 ft. deep, 3 rotation chambers, 3 settling tanks, gaging chambers and motor houses, and handles 500,000 imp. gal. per 24 hrs. Velocities of $1\frac{1}{2}$ ft. per second or higher are required. From 25 to 50 h. p. per mil. gal. per day are required. LANGDON PEARSE

Construction of Milwaukee activated sludge sewage disposal plant. R. R. LUNDAHL. *Munic. County Eng.* 63, 224-9(1922); *Can. Engr.* 44, 278(1923). L. P.

Activated sludge experiments at Glasgow. *Surveyor* 62, 173(1922).—Calcs. based on data given by Harris (cf. C. A. 17, 168) indicate a very much higher power consumption for the circulation scheme (Sheffield) than for the aeration scheme. The low power consumption at Sheffield may be due to the use of a well settled sewage. Fe compds. in the Sheffield sewage may also be advantageous in reducing the power requirements. P. W. MOHLMAN

Activated sludge for packing house waste at Mason City. EDWARD BARTOW. *Public Works* 53, 262-3(1922); cf. C. A. 17, 170.—The aeration unit is 39 ft. wide, 48 ft. long, 15 ft. deep, with a capacity of 155,000 gal. providing a detention of 9 hr. with a flow of 300,000 gal. per 24 hr. and 30% sludge return. A Door thickener 36 ft. in diam. settles the aerated liquor. LANGDON PEARSE

Nitrogen loadings of sprinkling filters as aid in design. S. A. GREELEY. *Eng. Contr.* 59, 123-4(1923).—A curve shows the relation between N loading and strength of sewage for 16 plants. LANGDON PEARSE

Land disposal of liquid sludge at Blackburn, England. ANON. *Public Works* 53, 263(1922).—Wet sludge from Dortmund tanks is pumped directly to land into distributing trenches. LANGDON PEARSE

Chlorinating sewage at Selma, N. C. ANON. *Public Works* 53, 263-4(1922).—

The sewage is coarse-screened, passed through a baffled tank to break up solids, and treated with Cl.
LANGDON PEARSE

Dangerous gas in sewage filters. A. J. MARTIN. *Public Works* 53, 263(1922).—A worker in a manhole in a contact filter was overcome by CO₂.
L. P.

Cost of operation and maintenance of Fitchburg, Mass., sewage disposal works 1916 to 1921. D. A. HARTWELL. *Ann. Report* 1921; *Eng. Contr.* 58, 159(1922); cf. *C. A.* 16, 776.—Av. cost for 6 yrs. has been \$10.86 per million gals. or \$0.30 per capita served.
LANGDON PEARSE

Bacillus coli and *Bacillus aerogenes* in swimming pools. MAX LEVINE and C. H. WERKMAN. *Eng. Contr.* 59, 98-9(1923).—Eosin methylene-blue agar is recommended for differentiation of contaminating organisms in swimming pools.
L. P.

Typhoid fever in the province of Milan. P. L. FIORANI. *Giorn. reale soc. italiana d'igiene* 1922; *L'Igiene moderna* 15, 182(1922); *Bull. mens. internat. office d'hyg. publ.* 14, 1437(1922).—Increase in typhoid was noted in 1921, an exceptionally dry year. In addition to the influence of the lowering of the water table in wells (Pettenkoffer theory) the use of polluted canal water for washing green vegetables and the utensils of the kitchen and the dairy are blamed.
JACK J. HINMAN, JR.

Ship fumigation. ANON. *Pub. Health Repts.* 37, 2744-7(1922).—Various gases which might control rodents and insects in ships were studied. CO is highly efficient but the app. necessary for its generation is too complicated. SO₂ is fairly efficient, but costly, harmful to certain articles and requires too long a time to act. HCN is highly toxic, cheap, requires a short exposure but, because it is practically odorless and non-irritating, is dangerous. The use of a mixt. of chloroacetophenone gas (tear gas) and HCN brought out the fact that the tear gas remained long after the HCN but the 2 gases tended to form pockets rather than uniform mixts. Since CNCl possessed the necessary toxic and lachrymating qualities, it was investigated and the following mixt. is suggested for its production: NaCN 113 g., NaClO₃ 85 g., talc 57 g., HCl sp. gr. 1.20 500 cc., H₂O 1 l. The talc is mixed with the NaClO₃, the NaCN is added and the bag contg. the mixt. is dropped into the dil. acid. This suffices for 100 cu. ft. of space. The talc reduces fire and explosion hazards to the safety point. The toxicity is high for rodents, bats, roaches and bedbugs, but the amt. necessary to kill lice has not been detd. The gas causes intense lachrymation, has high penetration and does not affect foods, fabrics, leather and metals except possibly Ni. It is probably less persistent than HCN. Expts. on ship ventilation as a means of clearing out the gas are underway.
CHAS. H. RICHARDSON

The comparative efficiency of the circular konimeter and the Palmer water spray apparatus for the determination of the dust content of the air. C. E. A. WINSLOW and ROBERT JORDAN. *J. Ind. Hyg.* 4, 375-9(1923).—The konimeter, which is an impingement method, involves the use of an air current of sufficient velocity to secure the retention of the fine dust particles on a circular glass coated with white vaseline. Counts are made with a microscope. The dust counts were 2-20 times as high as with the Palmer app., the finer the dust the greater the variation. Errors of sampling with the konimeter are not serious and it is superior to the Palmer app. in that it is portable and more economical in time and labor in sampling and counting. A revision of the standard methods for detg. atmospheric dust is suggested.
G. C. BAKER

The absorption of "cyclon" by various foodstuffs (JANSEN, *et al.*) 12.

LEYSSSENNE, FELIX: Les eaux en Champagne dévastée. Etude géologique, chimique et bactériologique. Reims: Impr. Claude Helny. 94 pp. Fr. 6.

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

Some chemical aspects of agriculture. E. HOLMES. *Chem. Age* (London) 8, 80-4(1923).—A general discussion of soil compn. and sterilization, N fixation, alkali soils, sources of phosphate, blast-furnace flue dust and destruction of pests.

J. J. SKINNER

Climatic soil types. I. DE V. MALHERBE. *S. African J. Ind.* 5, 291-8(1922).—This is a general discussion of the meaning of soil types and the factors which det. them. Chem. compn. is considered, with special reference to the silicates of Al but the principal emphasis is placed on temp., relative humidity and rainfall. Representative soils throughout the world are thus classified and particular attention is given to the soils of South Africa, for which the climatic data above mentioned are given.

N. KOPELOFF

Acid soil studies. III. The influence of calcium carbonate, calcium oxide and calcium sulfate on the soluble soil nutrients of acid soils. R. H. ROBINSON AND D. E. BULLIS. *Soil Science* 13, 449-60(1922).—Certain acid soils of Oregon respond to lime treatment, others do not. The object of this investigation was to ascertain the causes for these differences. Periodic detus. were made of the water-sol. nutrients of these soils after treatment with CaO, CaCO₃ and CaSO₄. All soils gave increased amts. of sol. K and Mg after treatment with CaSO₄. Water-sol. P₂O₅ and SO₃ were very low in all soils and showed no response after treatment. The main difference noted was in the formation of large amts. of NO₃ due to treatment with CaCO₃ and CaO in the soils that responded to liming. The other soils showed a much smaller increase. R. B.

"Reaction" of soil. U. PRATOLONGO. *Giorn. chim. ind. applicata* 4, 517-21 (1922).—This preliminary note reviews the fundamental concepts of soil "reaction," and comprises these topics: (1) alkalinity and inorg. acidity of soil, (2) processes of oxidation and reduction in the formation of soil acidity, (3) measure and expression of acidity and alkalinity of soil (*p_H* values and indicators), (4) classification of acid and alk. soils, (5) acidity and alkalinity of soil and their relations to bacterial flora and to vegetation, (6) agrarian treatment of acid and alk. soils. ROBERT S. POSMONTIER

Influences of salts on azofication in soil. J. E. GREAVES, E. G. CARTER, AND YEPFA LUND. *Soil Science* 13, 481-99(1922).—The Cl, NO₃, SO₄ and CO₃ salts of Na, K, Ca, Mg, Mn, and Fe are less toxic to azofiers in the soil tested than to ammonifiers and nitrifiers. The amt. of salt required to produce toxicity varied with the salt. No Na salt was toxic in concns. of 460 p. p. m. CaNO₃, CaSO₄ and CaCO₃ at 400 p. p. m., MgCl₂ and MgSO₄ at 243 p. p. m., Mn(NO₃)₂ at 550 p. p. m., FeCl₃ at 372 p. p. m. were not toxic. All salts studied except KCl, K₂CO₃, MnCO₃ and Fe₂(SO₄)₃ stimulated the activities of the organism at some concn. The presence of soil alkali in quantities sufficient to retard ammonification, nitrification and plant growth may not seriously retard azofication. R. BRADFELD

The mechanical analysis of soil containing heavy minerals. B. DE C. MARCHAND. *S. African J. Sci.* 18, 223-6(1922); cf. *C. A.* 16, 3996.—In mech. soil analysis the assumption is made that the different size particles have approx. the same sp. gr. Analyses of a soil are given for which this assumption does not hold. This soil contained magnetite ore, and it is shown from Stokes' law that in the sedimentation analysis the magnetite particles will ppt. with those portions of the common soil minerals which are 1.5 times their size. For particles larger than 0.2 mm. correction can be made by calcg. the quartz equiv. of the magnetite particles on the basis of their resp. sp. gr., or else by sepn. by means of Thoullet's soln. In all soils contg. abnormally heavy minerals,

these must be carefully considered when judging the soil from its mech. analysis.

F. W. ZERBAN

McHenry county soils. J. G. MOSIER, R. W. DICKENSON, H. W. STEWART, E. VAN ALSTINE AND H. J. SNIDER. Illinois Agr. Expt. Sta., *Soil Rept.* No. 21, 50 pp. (1921).—Chem. analyses of the principal soil types in the county are given. The peats run high in N and S and low in K. The Mg varies greatly in the different soil types.

J. J. SKINNER

Official definitions and standards for fertilizers. H. D. HASKINS, *et al.* *Cotton Oil Press* 6, No. 8, 31-2(1922).—The Report of the Committee on Definition of Terms and Interpretation of Results of the A.O.A.C. (1) Basic phosphoric slag should contain not < 12% total P_2O_5 and not < 80% of this should be sol. in 2% citric acid soln. (2) The word lime shall not be used unless the "lime" is in a form to neutralize soil acidity. (3) Manures shall be what the name indicates and not contain other materials.

H. S. B.

A new source of fertilizer. K. ADINARAYAN RAO. *Agr. J. India* 17, 476-82 (1922).—Megasse is proposed as a possible medium of N fixation with a view to introduce it as a cheap fertilizer after proper treatment. A few megasse samples averaged N 0.24, CaO 0.108, K_2O 0.25 and P_2O_5 0.142%. Samples of megasse were thoroughly dried in the sun, sampled and stored in jars. The samples were half satd. and inoculated with N-fixing organisms. At the end of two months the samples contained 1.39% N. The method here used may be extended to other wastes such as prickly pear, dry leaves, straw, sawdust, etc.

RUSSELL M. JONES

Some relations of arsenic to plant growth. I. JOHN STEWART. *Soil Science* 14, 111-8(1922).—The effects of salts commonly occurring in the soil on the soly. of Pb arsenate are reported. The soly. is 3 p. p. m. in distd. H_2O , 33.8 p. p. m. in tap H_2O , 183.8 p. p. m. in a mixt. of common salts of concn. equiv. to 0.1% K_2CO_3 , and 324.9 p. p. m. in the same mixt. of five times the above concn. In the single salt series, the sulfates and nitrates had but comparatively slight effect in all concns. The acid salts, bicarbonates, acid phosphates and especially the hisulfate had a very great solvent action. Salts which yield an alk. reaction on hydrolysis were also effective. The soil soln. dissolved Pb arsenate in amts. varying from 10 to 64 p. p. m. with the different soils studied. **II.** JOHN STEWART AND E. S. SMITH. *Ibid* 119-26.—Peas, radishes, wheat, potatoes and beans were grown in pots which received applications of from 0 to 500 p. p. m. (on basis of dry soil) of As after the plants were from 2 to 3 wks. old. 25 p. p. m. of As was stimulating to all crops; 75 p. p. m. was not injurious to some plants but the more sensitive ones, beans especially, were affected. The above applications are equiv. to about 125 and 375 p. p. m. of soil soln. The accumulation of As in the soil due to spraying if not continued in excess may be beneficial rather than injurious.

R. BRADFIELD

Notes on the fertilizing effects of potash. G. A. COWIE. *Chem. Age* (London) 8, 85-6(1923).—Potash serves as a preventive of a number of plant diseases and is often effective in increasing the vigor and resistance of the crop against unfavorable influences, chiefly climatic.

J. J. SKINNER

The value of ammonium chloride as nitrogenous fertilizer. J. KUYPER. *Arch. Suikerind.* 31, 1-4(1923).—In 26 field tests with sugar cane on different soil types in Java NH_4Cl gave generally as good results as $(NH_4)_2SO_4$. It is not deliquescent, which is an important advantage in the tropics; it is fixed in the soil almost as well as the sulfate. Conditions are favorable for the manuf. of the chloride in Java, from air N and sea salt.

F. W. ZERBAN

Ammonium sulfate-nitrate and urea as nitrogenous fertilizers. J. KUYPER. *Arch. Suikerind.* 31, 21-5(1923).—In 10 field tests on sugar cane in Java NH_4 sulfate-

nitrate gave as good results as $(\text{NH}_4)_2\text{SO}_4$ and urea was also found equal to it in 8 expts. The sulfate-nitrate is so hygroscopic that its use in the tropics would be excluded even if its manuf. had not been abandoned. Urea has the advantage of high N content (46%), but it is fairly hygroscopic and leaches readily from the soil. Further expts. are under way.

F. W. ZERBAN

Beneficial results from the inoculation of canning peas with legume bacteria. WM. H. WRIGHT. *Abstracts Bact.* 5, 9(1921).—The practical results from the inoculation of canning peas are influenced by numerous and varied factors. Use of lime and inoculation of poor acid soils increase the N content and help the maturity of the peas. The strain of bacteria used may be an important factor in the results obtained, whether the soil be poor or fertile. The amt. of inoculum is likewise an important factor. When peas have been grown on fertile soil for several years in the regular rotation, use of lime and inoculation with an efficient strain of legume bacteria increase the yield of green plants, make maturity of the crop more uniform, improve the desirable grades of peas, and increase both the yield and the N content of the crop; this is especially true if the soil be acid.

JOSEPH S. HEPBURN

The possibility of using town refuse as fertilizer. JOHN RUSSELL. *J. Ministry Agr.* 29, 685-91(1922).—Dry refuse from ash pits is described; analysis of the material from several cities gave N 0.39-2.13, P_2O_5 0.19-1.09, K_2O 0.3-0.64 and org. matter 13-37.5%.

J. J. SKINNER

Practical control of *Eleodes hispilabris* over an extensive area. C. WAKELAND. *J. Econ. Entomol.* 16, 96(1923).—A poison bait consisting of kiran, Paris green, amyl acetate and H_2O gave efficient control.

C. H. R.

A repellent for flat-headed borers. R. H. PETTIT. *J. Econ. Entomol.* 16, 97, 98(1923).—A repellent for borers in apple and other trees. Laundry soap 50 lbs., H_2O 3 gals., naphthalene 25 lbs., flour 2 lbs. Soften the soap (K base) for several days over steam pipes, then heat to 180°F ., add flour and naphthalene and heat again to 180° and cool. Apply with a brush after warming and thinning.

C. H. R.

Some recent experiments in the control of the cabbage maggot (*Chortophila, brassicae* Bouche). W. H. BRITAIN. *J. Econ. Entomol.* 16, 61-8(1923).—A comparison of HgCl_2 with this compd. mixd. with creosote, anthracene oil or tobacco dust showed that there was little difference in com. practice in the efficiency of the various treatments. Expts. showed that all the main classes of compds. entering into the compn. of creosote have a marked insecticidal or repellent value.

CHAS. H. RICHARDSON

Control of the root maggot in cabbage seed-beds. H. GLASGOW. *J. Econ. Entomol.* 16, 68-73(1923).—The HgCl_2 is favored by cost and adaptability over the method of covering the plants with cheese cloth. Of the other materials tested, only tobacco dust gave any promise of success.

CHAS. H. RICHARDSON

The onion capid, *Orthotylus translucens* Tucker. P. A. GLENN. *J. Econ. Entomol.* 16, 79-81(1923).—A spray of whale oil soap contg. 28 g. per gal. of H_2O will kill adults and nymphs instantly. Other mech. methods are described and the life history is given.

C. H. R.

Further data on fumigation with hydrocyanic acid gas in greenhouses on a commercial basis. E. R. SASSER AND C. A. WEIGEL. *J. Econ. Entomol.* 16, 84-7(1923).—An extension of work previously reported (*C. A.* 16, 3726).

C. H. R.

Results of spraying and dusting for the control of the red spider (*Paratetranychus pilosus*). D. M. DELONG. *J. Econ. Entomol.* 16, 88-90(1923).—The following combinations were used: S dust; S 90 parts, Pb arsenate 10 parts; S 75, Pb arsenate 10, lime 15; S with 15% nicotine, and S with 3% nicotine. These mixts. gave from 50 to 60% control. Sprays used for comparison gave the following: Lime-sulfur (1 to 65 or 75) gave good control, but was 5-10% more effective when resin fish oil or laundry

soap was added at the rate of 1 lb. to 50 gals. of the mixt. A soln. contg. 1% lime-sulfur soln., 6 lbs. S paste and 1 lb. resin fish oil soap per 100 gals. gave very satisfactory control.
C. H. R.

The insecticidal properties of tobacco dust. P. J. PARROTT AND H. GLASGOW. *J. Econ. Entomol.* 16, 90-5(1923).—Com. grades of tobacco dust vary greatly in nicotine content and phys. properties. Dust of 100-200-mesh killed a larger % of spirea aphid, current aphid and red bug than the coarser dusts. It was not uniformly as toxic as dusts contg. nicotine sulfate. The rosy aphid was controlled with tobacco dust or nicotine sulfate in lime-sulfur, glue-sulfur and cascine-sulfur sprays. These sprays were more efficient than dusts contg. tobacco dust or nicotine sulfate. Fine tobacco dust contg. 10% $\text{Ca}(\text{OH})_2$ or undild. had good phys. properties for dusting purposes. Pumps with poppet valves and coarse strainers were best for sprays contg. tobacco dust. Although at present concd. tobacco exts. are more economical than dusts, it is believed a use can be found for the dusts.
CHAS. H. RICHARDSON

Abundant but little known group of soil bacteria (CONN.) 11C.

EHRENBERG, PAUL: *Die Bodenkolloide*. 3rd Ed. revised and enlarged. Dresden and Leipzig: Th. Steinkopff. 717 pp. M 150, bound M 165.

MOHR, E. C. J.: *De grond van Java en Sumatra*. Amsterdam: J. H. DeBussy. Fl. 6.00. Reviewed in *Arch. Suikerind.* 31, 11-2(1923).

ORRO, R.: *Düngerlehre*. 3rd Ed. revised. Stuttgart: E. Ulmer. 86 pp.

Phosphatic fertilizer. H. PLAUSON. U. S. 1,445,167, Feb. 13. Slag phosphate is ground and then subjected to intensive mechanical disintegration in the presence of a large amt. of H_2O acidulated with H_2SO_4 or other acid, with or without heating or use of protective colloids.

Dissolving arsenious oxide with caustic soda. J. F. CULLEN. U. S. 1,448,160, Feb. 20. A concd. As_2O_3 soln. adapted for use in making insecticides is prepd. by dissolving As_2O_3 in a soln. of NaOH and subsequently cooling the soln., using such proportions that after cooling the mol. ratio of the As_2O_3 to NaOH in the soln. exceeds 1:1.

16—THE FERMENTATION INDUSTRIES

C. N. FREY

What happens during fermentation? F. F. NORD. *Chem. Met. Eng.* 28, 351-3 (1923).—Alc., AcOH and butyric acid fermentation and the fermentation of sugar by *B. coli* were studied. Yeast is able to split sugar into alc., AcH, glycerol and CO_2 although sugar contains no Et or CO_2 groups. Fermentation reactions of yeast are dependent on the activity of zymase and carboxylase. The expts. of Connstein and Ludecke showed that glycerol could be produced from sugar in con. quantities provided, as shown by Bunte and later by Kerpe, AcH is removed by means of sulfite. Na_2CO_3 and Na_2HPO_4 were not suitable as they favored lactic fermentation. Na_2SO_3 does not inhibit fermentation and acts as an antiseptic. As high as 25% of the sugar fermented may be transformed into glycerol. Neuberg and Reinforth state that sugar and sulfite enter into loose combination which is dissociated in H_2O but part of the resulting complex, AcH, combines with sulfite to form a more stable combination. The ratio of glycerol formed to AcH is always 1:1. The fermentation reaction may be represented as follows: $\text{C}_6\text{H}_{12}\text{O}_6 + \text{M}_2\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CHOHOSO}_2\text{M} + \text{MHCO}_2 + \text{C}_3\text{H}_8\text{O}_2$. The generation of AcH and glycerol from sugar proceeds by the formation

of methylglyoxal-aldol which breaks down into an intermediate product, $2\text{CH}_3\text{COH}\cdot\text{COH}$, from which are derived methylglyoxal, glycerol, and pyruvic acid, the latter yielding CO_2 and AcH . Methylglyoxal reacts with AcH and H_2O to form pyruvic acid and alc. In normal alc. fermentation the final phase is a reduction of AcH to alc. By fixing AcH in the form of a sulfite complex, $\text{CH}_3\text{CHOHOSO}_2\text{M}$, it is withdrawn from the final phase of hydrogenation and, as free H is not liberated, glycerol is formed. The whole series of reactions are based on the assumption that initially 2 mols. of H_2O are split off from sugar to form methylglyoxal, the other reactions between methylglyoxal and AcOH having been detd. experimentally by transforming 2 aliphatic aldehydes and also by bringing about transformation between an aliphatic and aromatic aldehyde in the presence of a suitable catalyst. To test the theory further dextrose and glycerol fermentations by *B. coli* were studied by using CaSO_3 , Na_2SO_3 being toxic. AcH is an intermediate product, 40 to 50% of the corresponding alc. being formed. AcH is also present as an intermediate product in fumaric, citric, and putrefactive fermentations. The fermentation of sugar by yeast and *B. coli* is an anaerobic process. Light on aerobic fermentation was obtained by studying the reactions involved in wine and vinegar fermentation by *B. ascendens* and *B. pasteurianum*. From $1/3$ to $1/4$ of the AcOH formed during fermentation could be removed in the form of AcH . By growing *B. butyricus* Fitz in the presence of Na_2SO_3 11.8% of the aldehyde has been shown to have been formed. In the presence of sulfites *B. butyricus* reacts with AcH and its aldol to form alc. and AcOH instead of butyl alc. and butyric acid. Pyruvic acid is utilized as a source of C, but only traces of butyric acid are formed. α -Keto- γ -valerolactone- γ -carboxylic acid, the aldol of pyruvic acid, yields large amts. of butyric acid when fermented by *B. butyricus* Fitz. Sugar is transformed to $2\text{CH}_3\text{COCOOH} + 4\text{H}$; aldolization of the acid takes place, one reaction (a) yielding CO_2 and butyric acid and the other (b), a reaction between H and the aldol, yielding CO_2 , H_2O and butyl alc. Aldehydes may also be concerned as intermediate products in physiol. processes. The presence of AcH in such large amts., 75% of the alc. in sulfite fermentation, cannot be explained by assuming that some secondary oxidation of alc. occurs during fermentation.

C. N. FREY

Sugar fermentation in the presence of sodium sulfite according to Neuberg and Reinfurth. H. GEHLE. *Biochem. Z.* 132, 566-88(1922).—An increase in the concn. of Na_2SO_3 in the fermenting mixts. is accompanied by an increase in the disarrangement of the fermentation products. This displacement almost stops when the sulfite present is 60% of the sugar. This is attributed to the alterations in OH^- ion concn. The use of different yeasts is without influence on the qual. or quant. make-up of the fermentation products. The only difference is the response to the toxic effect of the Na_2SO_3 , and consequently the amt. of protein glycerol undergoes more or less change as a measure of the vital activity of the yeast. The protein glycerol is a product of the internal metabolism of the cells which is only indirectly influenced by the changes on the cell periphery. Detns. of the aldehyde, glycerol, alcohol and CO_2 account for 80-83% of the sugar; if acetic acid is detd. from 85 to 90% is accounted for. A comparison of the CO_2 evolution with increasing Na_2SO_3 concns. shows the fermentation intensity tends to be normal in the lower concn. and towards an earlier max. as the concn. increases. The results of higher concns. show that the yeast attempts to obviate the toxic effect by a regulative inhibition of diffusion.

F. S. HAMMETT

Action of ultra-violet rays upon *Saccharomyces cerevisiae*. ROMOLO AND REMO DE FAZZI. *Giorn. chim. ind. applicata* 4, 463-4(1922).—Industrial scale tests confirm benefits found in the lab. in the use of yeast which had been previously treated with ultra-violet rays.

ROBERT S. PUSMONTIER

The acidification of distilled vinegar mash by the Pasteur procedure. H. WÜSTEN-

FELD. *Deut. Essigind.* 26, 263-5(1922).—The typical quick vinegar bacteria from generators will slowly produce vinegar in vats contg. unagitated distd. vinegar mash of high concn. at 16-24°. The loss during the process is traceable to the alc. evapn., which is considerable if the fermentation is carried out in vats with open vent holes or with unhindered air excess due to ill-fitting covers. The loss takes place before the formation of the film on top of the liquid and at the beginning of the fermentation. It is small after the film forms and acetification begins. The loss of acid itself is slight compared to that due to evapn. of alc.

H. A. LEPPER

SIMMONDS, C.: Alcohol in Commerce and Industry. London: Sir Isaac Pitman Sons, Ltd. 119 pp. 3 s. Reviewed in *Nature* 111, 181(1923).

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Chemotherapeutic antiseptics. III. A new antiseptic, 2-ethoxy-6,9-diamino-acridine hydrochloride (Rivanol). J. MORGENROTH, R. SCHNITZER, AND E. ROSENBERG. *Deut. med. Wochschr.* 47, 1317-20(1921).

S. AMBERG

Albertan, a new antiseptic. C. BACHEM. *Münch. med. Wochschr.* 69, 312(1922).—Descriptive.

S. AMBERG

The arsenical solution. I. Liquor potassii arsenitis (Fowler's solution). H. A. LANGENHAN. Univ. Wisconsin. *Trans. Wisconsin Acad. Sci.* 20, 141-97(1921).—An historical review of the prepn. and use of this drug.

A. L. BARKER

Explosion in the preparation of oxycyanatum hydrargyrum. D. VAN OS. *Pharm. Weekblad* 60, 102-6(1923).—An account of an explosion that occurred in the factory of the Koninklijke Pharmaceutische Handelsvereniging in Amsterdam during the prepn. of a 5-kg. lot of mercuric oxycyanide. The dry product was being pulverized when the mass exploded, scattering a dark green powder 2-3 m. around the mortar. No casualties resulted.

A. W. DOX

Estimation of codeine. H. E. ANNETT AND R. R. SANGHI. *Analyst* 48, 16-8 (1923).—The present method is an improved form of that previously described (cf. C. A. 14, 3497). Triturate 8 g. of opium with 2 g. slaked lime and 80 cc. of H₂O during 1/2 hr., as in the Brit. Pharm. (1914) process. Ext. 50 cc. of the filtrate (= 5 g. opium) with 3 successive 50 cc. portions of PhMe, the latter being then passed through a dry filter into a distn. flask. Conc. under diminished pressure to a small vol. (about 25 cc.), then bubble HCl gas through for 1/2 min. Filter off the flocculent codeine-HCl on a dry filter, dissolve in H₂O and pass the aq. soln. through the same filter into a small round-bottomed glass dish, a deep magenta color developiog. Evap. on the H₂O bath until almost dry, then transfer to a H₂O oven and dry to const. wt., thereby rendering the coloring matter insol. in H₂O. Treat the substance with hot H₂O, transfer to a graduated 50 cc. flask, make up to mark, add 0.2 g. freshly slaked lime and shake during 1/2 hr. Filter, ext. 40 cc. of the filtrate with 3 successive 40 cc. portions of PhMe, filtering each portion through a dry filter into a distg. flask as before, and finally wash the filter with a small amt. of fresh PhMe. Cooc. the liquid to a small vol. as before, then treat with dry HCl for 1/2 min. Filter, dissolve the ppt. in H₂O, passing the resulting liquid through a filter into a small weighed round-bottomed glass dish. Evap. almost to dryness, add a little dil. EtOH to encourage crystn., dry to const. wt., calc. the residue as the hydrochloride plus 1.5 mols. H₂O crystn.

W. O. E.

Standardization of perfumers' raw materials. F. K. WOODWORTH. *Chem. Age* (N. Y.) 31, 36(1923).—A plea for such practice, as followed in most other industries.

W. O. E.

Santoperonia. A. MARX. *Chem.-Ztg.* 47, 81-2(1923); cf. C. A. 16, 2960; 17, 612. Polemical. W. O. E.

Hypochlorite solution and "antiformin." E. O. RASSER. *Chem.-Ztg.* 47, 37-8 (1923).—A discussion of the methods of prepn. and of the character and application of the finished products. W. O. E.

Santoperonia. BODINUS. *Pharm. Ztg.* 68, 68(1923).—A reply to Marx (cf. C. A. 17, 612). W. O. E.

History of capillary analysis in the pharmacy. H. PLATZ. *Pharm. Ztg.* 68, 77 (1923).—Controversial, with especial reference to Wachtel (cf. C. A. 17, 1300). W. O. E.

Curare and a new method for its production. L. LEWIN. *Chem.-Ztg.* 47, 65-6 (1923).—The present paper represents L.'s conclusions formed from investigations of arrow poisons over a period of several decades. The various brands or sorts have been arranged, irrespective of form or container, into 2 classes, namely: (1) clay-colored to brown, and (2) brownish black to black curare, between which a regional (equatorial) line of demarcation appears to exist. While a product, uniform in the generally accepted sense, is impossible of prepn. on account of the wide variations in the quality and quantity of its several constituents, L. has nevertheless attempted the production of a curare (curarine) possessing a certain constancy in av. activity, and employing as raw materials 2 widely varying sorts, the one (almost black and completely sol. in H_2O) a calabash curare from Guiana, the other (brownish, moderately sol. in H_2O) a tube curare from the upper Marañon. Both received the following treatment. Dissolve to the utmost in warm H_2O , macerate the soln. with freshly pptd. PbO for a considerable period, then dry completely at a moderate temp., finally *in vacuo* to a const. wt. Exhaust the finely powd. material with abs. EtOH in connection with a reflux during several days. Evap. the solvent completely, macerate the residual ext. with warm H_2O till nothing further dissolves, treat with H_2S to remove traces of Pb, then evap. the clear filtered soln. to dryness at not to exceed 50° , finally *in vacuo* to const. wt. The resulting varnish is powdered, dissolved in cold abs. EtOH, and pptd. with Et_2O , filtered by suction on a porous plate, washed with Et_2O and dried. Thus prepd. the curarine is a brown to grayish yellow, non-hygroscopic powder, readily sol. in warm EtOH, and sol. in H_2O yielding a neutral soln. With the alkaloidal reagents (excepting Selmis') it yields ppts., even in aq. soln. contg. only 0.0005 g. substance. HPO_3 produces no ppt. in aq. soln.; KI on the contrary does. $Ti-H_2SO_4$ reagent yields a violet stain; $K_2Cr_2O_7$ and H_2SO_4 are without effect. It dissolves in warm EtOH and tastes bitter. Complete paralysis in the frog was effected after subcutaneous injection of 0.005 g. curarine in 3 min., with 0.0005 g. in 5 min., with 0.00005 g. in 10 min. The use of curarine thus prepd. as a medicament is suggested. W. O. E.

Relationship between oil glands and oil yields in the eucalypts. M. B. WRIGHT. *J. Proc. Roy. Soc. N. S. Wales* 56, 149-52(1922).—It appears from a study of W.'s findings that while the theoretical values for certain species with small yields agree fairly well with the actual yields, this is not the case in the majority of species, and there is such a wide variation, notably in *E. aggregata* and *E. rubida*, that it is impossible from such detns. to predict accurately what the approx. yield of oil will be. W. O. E.

Aldehydes, their odors and their uses. A. ST. PFAU. *Perfumery Essent. Oil Record* 13, 382-4, 422-4(1922); 14, 12-4(1923).—A review of the role aldehydes play in the perfume industry. Of the 33 aldehydes of known structure discovered in essential oils, all except the 5 lowest aliphatic members find application. Of these only the terpene aldehydes are actually prepd. from natural sources, the others being more easily accessible artificially. At least an equal no. of purely synthetic members not yet found in nature are used in greater or less quantity, most of them being brought

upon the market in the form of compds. The importance of aldehydes extends beyond this. Many synthetic perfumes are obtainable from them. Certain new methods enable the aldehydes to be prepd. in quant. yield, so that substances formerly obtained from other sources may now be prepd. from aldehydes. *E. g.*, (a) primary alcohols and their esters: $\text{CHO} \rightarrow \text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{OX}$. The catalytic reduction of the aldehyde is quant. Thus citral \rightarrow citronellol \rightarrow citronellyl acetate; $\text{PhCH}_2\text{CHO} \rightarrow \text{PhCH}_2\text{CH}_2\text{OH} \rightarrow \text{PbEt } n\text{-butyrate}$. (b) Acids and their esters: $\text{CHO} \rightarrow \text{COOH} \rightarrow \text{COOR}$. The oxidation is effected with O in the presence of a catalyst such as a Mn salt. Thus, citronellal gives Et citronellate; cuminaldehyde gives Me cumate. (c) Ketones with 3 additional C atoms and their dihydro compds.: $\text{CHO} \rightarrow \text{CH:CHCOMe} \rightarrow \text{CH}_2\text{CH}_2\text{COMe}$. The condensation with excess acetone in the presence of alkali is practically quant., and the subsequent reduction proceeds here with especial ease. Thus, oenanthaldehyde yields Me octenylketone and thence Me octyl ketone; vanillin gives vanillalacetone and by reduction zingerone. W. O. E.

Machine-made lemon oil. I. W. G. UNCERER. *Perfumery Essent. Oil Record* 14, 3-5 (1923).—U. reviews the method in common practice in and about Messina which influences the production, quality and price of the Italian lemon oil. He clearly favors the "sponge" method of Sicily and emphasizes the apparent fact that chem. analysis is of but little assistance in indicating the influence of the various factors affecting quality. This being so, the buyer must fall back on his experience as an aromatican. U. defines the desired product as "a carefully selected virgin oil manufactured from perfectly sound ripe fruit without any admixture of any sort for any purpose, and possessing the full fresh bouquet of well matured fruit." II. A. C. SUTTON. *Ibid* 5-6.—S. takes decided issue with certain of U.'s views relative to the essentials requisite for the production of a high-grade oil. He favors the machine-made product as obtained in Calif. in the form of "a perfectly clear, brilliant, and highly colored oil ready for filling off into actual shipping containers within 16 min. from the time the fruit enters the app." S. agrees with U. that chem. analyses are of little value in evaluating the commodity, likewise with U.'s specification for a lemon oil. III. F. J. BAKER. *Ibid* 6-7.—Issue is taken with S.'s statements. On the basis of some 8 years' experience in the Messina district, it is asserted that there is not a machine in existence that produces a lemon oil equiv. to a sponge oil. It is claimed that the oil (machine-made), being in a fine state of division in the juice, loses something, and part of that something is citral, besides other essential ingredients. At the same time something is taken out of the juice that ought to remain. Part of that is wax or resin from the skins and coloring matter. The flavor, or the bouquet, of the machine oil is not that of ripe mature lemons, but of over-ripe fruit, and therein lies a vast difference. U.'s description of lemon oil is endorsed. Herein all 3 authors agree. W. O. E.

Alteration of lemon oil on keeping. G. H. OGSTON AND MOORE. *Perfumery Essent. Oil Record* 14, 7 (1923).—In June 1913 a sample was taken in duplicate from a consignment of lemon oil, one analyzed at once, the other tightly corked, sealed and packed in a sample case and held in reserve till Jan. 1923 when it also was examd. A comparison between the original and the present analyses shows, resp., d_{40}^{20} 0.8585, 0.8589; optical rotation 58.35° , 58.45° ; non-volatile residue 2.52%, 2.93%; citral 3.90%, 3.60%; esters, 2.50%. It would appear, therefore, that lemon oil can be kept for many years in suitable containers away from the light and in the absence of air without suffering material impairment as to quality. W. O. E.

Anthranilic acid and some of its esters. L. G. RADCLIFFE. *Perfumery Essent. Oil Record* 14, 10-2 (1923).—Based upon the Brit. pat. 18,246, Nov. 12, 1890, the prepn. of the acid from phthalimide is described, then from the acid certain of its esters, notably the Me and Et esters. Their application to perfumes, as also some of their chem. reactions, is discussed. W. O. E.

Dry antiseptics. I. LOEWY. *Pharm. Monatsh.* 4, 4(1923).—Mention is made of the new CHI_3 substitute, *vulmodermol*, a product alleged to have elementary I in physical combination, yielding this element only slightly to the atm., but gradually and continually mobilizing it under the influence of wound and mucosa secretions.

W. O. E.

Culture of medicinal plants and attempts to increase their active principles. A. TSCHURCH. *Pharm. Monatsh.* 4, 4-5(1923).—An address. Cf. C. A. 16, 2387.

W. O. E.

Ergot. A. STOLL. *Pharm. Monatsh.* 4, 5-6(1923).—An address. Cf. C. A. 16, 3171.

W. O. E.

Production of potassium iodide from iodized titration residues. R. BAUER ANN R. SCHALLER. *Pharm. Zentralhalle* 64, 17-9(1923).—A procedure is outlined for recovery, first of the I by steam distn. of the combined residues in the presence of free HNO_3 , and second conversion of the I to KI by treatment with Fe and K_2CO_3 .

W. O. E.

Chloramines. ANON. *Pharm. Ztg.* 68, 87-8(1923).—A discussion of the relative merits of both hypochlorites and chloramines.

W. O. E.

Dermatol plaster. H. POPP. *Pharm. Ztg.* 68, 88(1923).—Reference is had to certain adhesive plasters of recognized value contg. dermatol. Attention is particularly directed to "traumaplast" a brand alleged to contain dermatol, but found to be practically free from this substance. It contained some dyestuff, possibly thiazole yellow.

W. O. E.

Estimation of free phosphorus in phosphorized oils. P. BOHRISCH. *Pharm. Zentralhalle* 64, 43-6, 55-7(1923).—A discussion of the principal methods hitherto suggested or employed for the purpose in question, notably that recently published by Frey (cf. C. A. 17, 181), a modification of Euell's procedure. A study of Frey's method in the hands of several analysts showed it to yield too high values, for which reason B. inclines toward retention of the original Euell procedure as the most dependable.

W. O. E.

Evaluation of drugs. GEORG FROMME. *Pharm. Zentralhalle* 64, 57-60(1923).—A discussion of improvements in drug methods with special reference to F.'s experience in the evaluation of cinchona bark.

W. O. E.

Estimation of albumose silver. J. HERZOG. *Pharm. Ztg.* 67, 802-3(1922).—In a 200 cc. Erlenmeyer flask dissolve 1 g. of the sample in 10 cc. of H_2O , add in a thin stream with const. agitation 10 cc. of concd. H_2SO_4 , and follow likewise with vigorous shaking with 2 g. finely powd. KMnO_4 in minute portions. After standing 15 min., dil. with 50 cc. of H_2O , add FeSO_4 in small portions until a clear almost colorless soln. results, then titrate with 0.1 N NH_4CNS to the appearance of a rusty yellow color.

W. O. E.

Piperitone in eucalyptus oils. A. R. PENFOLD. *Tech. J. (Australia)* 1, No. 1, 11-2 (1922).—On account of the prominence recently accorded to piperitone due to its ready conversion into thymol and menthone, P. has studied its detection and estn. in eucalyptus oils, more particularly its sepn. from *E. dives*, the oil of which usually contains 40 to 50%, indeed in certain cases as high as 64% piperitone. **Detection.**—Mix 1 cc. of the oil of *E. dives* with 1 cc. MeOH and 4 cc. of Et_2O , then add 1 g. of 3% NaHg. If piperitone is present, a reddish brown color immediately develops, and at the end of about 10 min. a copious white ppt. separates, the pinacone, $\text{C}_{15}\text{H}_{24}\text{O}$, m. between 142 and 149°. By fractional pptn. from CHCl_3 this substance can be sepd. into 2 compds. m. 135-6° and 166-7°, resp. **Estimation.**—Pipet 5 cc. of the oil into a cassia flask of about 150 cc. capacity (neck graduated in 0.1 over a 5 cc. range), add a soln. of crysd. Na_2SO_4 (350 g. in 1000 cc.) to fill about $\frac{1}{3}$ of flask, and heat contents in a *rigorously*

boiling H₂O bath, with const. agitation. Neutralize the liberated alkali from time to time by means of 10% AcOH soln. until the reaction is complete. Gradually make up to vol. with the sulfite soln., finally forcing the unabsorbed oil into the neck of the flask, which may be read off when cold. The difference in vol. between the unabsorbed oil and the original 5 cc. represents the amt. of piperitone present; this multiplied by 20 gives the %. *Separation from E. dives*.—Two methods, available for works' practice, give good results, viz.: 1. (a) Subject the crude to distn. in a pot still and collect the portion boiling below 220° (or b₁₀ 100°) separately (principally phellandrene). The piperitone will be found in the 2nd fraction b. 221–36° (b₁₀ 100–12°). (b) In the absence of vacuum distn., the residue freed from the phellandrene may be subjected to fractional steam distn., the process being controlled by the refractometer. 2. Instead of direct distn., provided the oil contains not less than 48% of piperitone, the phellandrene can be removed by a rapid current of steam, after which the piperitone is obtained by either (a) or (b). *Summary of chemistry of piperitone*.—b_m 229–30°, b. (corrected) 235°; d₁₅ 0.9393, d₂₀ 0.9348; (α)_D –0.4 to –50.2°; n_D²⁰ 1.4837; oxime m. 117–8°; semicarbazone α m. 225–6°, β 175–6°, β-racemic 188–9°; benzylidene deriv. m. 61°; bisnitroso deriv. m. 96–7°. Na in aq. Et₂O reduces piperitone to menthol, a pinacene and resinous products. H on the other hand yields, in the presence of Ni, menthone. On oxidation with FeCl₃ in AcOH soln. thymol is formed, while KMnO₄ leads to the formation of diosphenol, α-hydroxy-α-Me-α-isopropyladipic acid, α-isopropyl-γ-acetylbutyric acid, and α-isopropylglutaric acid. W. O. E.

A chemical examination of a Venezuelan jaborandi. O. F. BLACK, J. W. KELLY AND W. W. STOCKBERGER. *Am. J. Pharm.* 95, 4–7(1923).—The Venezuelan species has not only a much smaller percentage (0.25%) of total alkaloids than *Pilocarpus jaborandi*, but the percentage of pilocarpine (0.04%) is also very much less. However, it compares favorably with several other species, namely *Pilocarpus spicatus*, *P. trachylopus*, and *P. pennatifolius*. There is little reason to doubt that the poisonous effect of Venezuelan jaborandi on livestock is due to the alkaloids present in this species since the symptoms recorded by Ernst (*El Ensayo Medico* 1, No. 8, 61–2(1883)) are among those recognized as evidence of pilocarpine poisoning. W. G. GAESSLER.

The amounts of anthracene derivatives in different sennas. E. MAURIN. *Bull. sci. pharmacol.* 29, 617–22(1922).—The cultivation of senna is good practice since the purgative value of preps. is not diminished while the purity of the product is increased. The senna of Alexanuria is better than Indian senna. Freshly harvested material should be used. An infusion of the drug contains less free anthraquinones than does the decoction. F. S. HAMMETT.

The action of the germicide "Listol." ERNESTO CROSONINI. *L'Igiene moderna* 13, 257(1922); *Bul. mens. office internat. d'hyg. publique* 14, 1565(1922).—"Listol" is an Argentine mange remedy. It is a heavy reddish brown liquid with a characteristic odor, mixing with equal pts. glycerol and alc., and perfectly sol. in water. It is slightly alk. but has no caustic effect on wounds in 3 to 5% soln; does not attack metals readily, and is without action on wood, marble, brick, cloth, leather or varnish. It kills pathogens in 1/4 to 1/10 the time required for phenol solns. of the same strength.

JACK J. HINMAN, JR.

Artificial essential oils. G. MONTI. *Riv. ital. ess. prof.* 4, 68–9(1922); *Chimie et industrie* 9, 126–7(1923).—Artificial oil of roses consists of a mixt. of geraniol, citronellol, linalool, phenethyl alc., etc., in varying secret proportions. A process giving exceptionally fragrant products consists in steam distg. these mixts. over rose petals (as in the extrn. of natural oil of roses). The perfume is almost identical, as also the solidification point and the proportion of stearoptenes. This result can also be obtained by adding about 10% of spermaceti or of natural stearoptene of roses. A simple formula is:

geraniol 70, citronellol 25, phenethyl alc. 5. A higher grade product is made from: geraniol 70, citronellol 15, linalool 7, phenethyl alc. 5, octyl aldehyde 0.1, nonyl aldehyde 0.1, decyl aldehyde 0.1. Various mixts. can give the odors characteristic of the different species of roses. Extremely pure products must be used. *Artificial jasmine*.—A product with a jasmine-like odor can be prepd. as follows: Heat on the water bath 50 g. of phenylglycol, 300 g. of H_2O , 25 g. of H_2SO_4 , and 100 g. of CH_3O ; ext. the light oil which forms with Et_2O , and rectify *in vacuo*. The compd. with jasmine-like odor seems to be $CH_3CH_2CH_2OCH_2$. The following is a practical formula for the prepn. of arti-

cial jasmine: Me anthranilate 50, BzOAc 200, indole 8, BzOH 600, linalool 100. The following formula is suitable for handkerchief perfume: artificial jasmine 10, natural abs. oil of jasmine 5, 5% infusion of natural musk 2, oil of musk-seeds 0.10. A. P. C.

Adulteration of lemon essence with terpenes. GUIDO AJON. *Giorn. chim. ind. applicata* 4, 389-91 (1922).—The value of lemon essence depends upon its citral content, which is usually about 4%. The analysis of lemon essence for purity is supposedly an analysis of the amt. of citral, but is really a detn. of the amt. of CO compds. This fact makes possible the adulteration of lemon essence with lemon terpenes (the more volatile products of the essence, obtained abundantly as by-product in working concentrates) and addn. of sufficient citral to bring the content in citral of the mixt. up to normal. But the essence so adulterated will lack the proper aunts. of the oxygenated compds. which give to genuine essence its characteristic delicacy of perfume. A.'s method is: distil the essence in question, collect from 5 to 10 fractions and det. the amt. of citral in each by Kleher's method. The first fraction of an adulterated essence will show higher figures for citral than the corresponding fractions of a genuine essence, while the later fractions will show lower figures.

ROBERT S. POSMONTIER

The new pharmacopoeia of Japan. ANON. *Chemist and Druggist* 97, 289-90 (1922); cf. C. A. 16, 4013.

S. WALDBOTT

Clary sage (*Salvia Sclarea* L., sweet clary). M. FLORIANZ. *Chemist and Druggist* 97, 445 (1922).—The flowers of this plant, used as an old tonic remedy in France, and as a flavor for vermouth in Italy, yield a distinctive essential oil (cf. C. A. 3, 2853) that may be used in perfuming soaps. Gattefossé produced a hybrid of this plant, named *S. Turquestiana*, whose essential oil has quite a strong musk aroma. S. WALDBOTT

Composition of Nectandra coto. HARVEY A. SEIL. *J. Am. Pharm. Assoc.* 11, 904-6 (1922).—The bark was so full of resin that it could be ground only with difficulty. The bark yielded 12.69% to petr. ether, of which 1.89% was ethereal oil. The petr. ether-extd. bark yielded 10.25% to Et_2O and later 8.02% to $EtOH$. The petr. ether ext. contained most of the cotoin. The $EtOH$ ext. contained most of the tannin and alkaloids. Total alkaloids are 1.38% of which 0.60% has phenolic properties. The non-phenolic alkaloid is named *parostemine* and the phenolic alkaloid *parosteminine*. Parostemine gives a crvst. ppt. with $KHgI_3$ reagent and KI + I. Parosteminine gives a purple-red color with $FeCl_3$ in $EtOH$. The bark yielded 1.67% ash.

L. E. WARREN

The seeds of Bixa orellana. S. S. AYAR. *J. Am. Pharm. Assoc.* 11, 999-1003 (1922).—*Bixa orellana* is related to *Taraktogenos kurzii*, the source of chaulmoogra oil. These seeds are the source of annatto. The ground, red seeds were distd. with xylene to det. H_2O . Moisture was 3%. The hot solvent dissolved some of the yellow dye and deposited it on cooling. Total ash was 4.77, acid-insol. ash 2.35, Et_2O ext. 2.55, heptane ext. 2.8, $EtOH$ ext. 0.9%. Patty oil was prepd. by extrn. and distn. under 8-12 mm. Sapon. no. was 166, I no. 116.6, acid no. 117.9, $[\alpha]_D^{20}$ 0°, d_4^{20} 0.914, m. 290°. Chaulmoogric acid was not found. Oleic acid, palmitic acid and stearic acid were probably present. A trace of volatile oil was present.

L. E. WARREN

Refractive indices and their temperature coefficients (THOMPSON) 2.

BOHLMANN: Code chimique. En combinaison avec le livre d'adresses de l'industrie allemande des produits chimiques. Paris: G. Ficker. Fr. 100.

GANSWINDT, ALBERT: Die Riechstoffe. 8th revised Ed. Leipzig: Bernh. Friedr. Voigt. 362 pp. M 150, bound M 200.

ROSSI, A.: Il profumiere. 3rd Ed. Mailand: U. Hoepli. 665 pp. L. 26.

SCHNEIDER, J.: Biochemischer Hausarzt. 4th revised Ed. Leipzig: W. Schwabe. 348 pp.

Year-Book of Pharmacy 1922 and Transactions of the British Pharmaceutical Conference, Nottingham. London: J. & A. Churchill. Reviewed in *Chem. News* 125, 368(1922).

n-Butyl *p*-aminobenzoates. R. AOAMS and E. H. VOLWILER. U. S. 1,440,652. Jan. 2. *n*-Butyl *p*-nitrobenzoate (white plates, m. 35°) is prepd. by reaction between BuOH and $O_2NC_6H_4CO_2H$ in the presence of H_2SO_4 . After sepn. and purification it is reduced with Fe and HCl to butyl *p*-aminobenzoate, which is extd. with ether from alk. soln., recovered by evapn. and crystd. from H_2O or petroleum ether, m. 57-58.5°. It is a local anesthetic, the effect of which is more lasting than that of some related anesthetic compds. Bu 3,5-dinitrobenzoate is similarly reduced to Bu 1,3,5-diaminobenzoate, a viscous liquid which does not solidify at room temp. When an ether soln. of the latter is treated with alc. HCl, a white solid monohydrochloride is formed, m. (decompn.) 255°.

Diaminodihydroxyarsenobenzene-silver oxide compound. A. E. SHERNDAL. U. S. 1,446,216, Feb. 20. A Ag compd. substantially free from toxic inorg. salts is obtained by reaction of Ag_2O on the di-Na salt of diaminodihydroxyarsenobenzene and pptg. with alc. The Ag compd. is a brown powder, sol. in H_2O , suitable for therapeutic use.

Arsonoacetic acid. J. HUISMANN, J. CALLSEN AND W. GRÜTTFERN. U. S. 1,445,685, Feb. 20. $H_2O_2AsCH_2CO_2H$ is prepd. by reaction of H_2SO_4 on Ca salt prepd. from As_2O_3 , chloroacetic acid, NaOH, HOAc, NH_4OH and $CaCl_2$, successively added. The acid crystallizes from glacial HOAc as hard colorless crystals, m. 152°, almost insol. in acetone, C_6H_6 and ether, easily sol. in H_2O and in alc. Both the salts and the free acid are adapted for therapeutic use internally or by intramuscular injections.

Dentifrice. C. PFANSTIEHL. U. S. 1,445,351, Feb. 13. A tooth-cleaning paste is formed of pptd. $CaCO_3$, anhydrous glycerol, absolute alc. and galactonic lactone (as a solvent for the binder of tartar).

Dentifrice. C. PFANSTIEHL. U. S. 1,445,352, Feb. 13. A paste-like dentifrice is formed from tri-Ca phosphate 40-75%, a soln. of galactonic lactone 1-4 and galactonic acid in H_2O 8-18, gum arabic or gum tragacanth, glycerol 8-25 and alc. 5-15%.

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FREO C. ZEISBERG

Fractionation of nitric acid. J. BAUMANN. *Chem.-Ztg.* 44, 678(1920).—By distg. 69.8% HNO_3 (sp. gr. 1.4), a dephlegmator heated to 100° being used, equal vols. of distillate contg. 0.02% of HNO_3 and of residue contg. 69.5% were obtained. Distn. of 500 cc. 91.5% acid, a dephlegmator heated at 86° being used, yielded 140 cc. of 70.1% acid (the const. boiling mixt.) and a residue of 350 cc. of 100.5% acid.

J. S. C. I.

The production of sulfur dioxide from the alkaline earth sulfates and iron or iron

sulfide. F. MARTIN AND O. FUCHS. *Z. anorg. allgem. Chem.* 125, 307-48(1923).—The sulfates of the alkaline earth elements are reduced to sulfides by heating with Fe at temps. lower than those required for reduction with C. Complete reduction is obtained in 30 min. at 750° for CaSO_4 ; 850° for SrSO_4 and 950° for BaSO_4 . If insufficient Fe is present for complete reduction and if the temp. is about 150° higher, SO_2 is evolved. The best yield of SO_2 results when a definite amt. of Fe is used. For CaSO_4 this corresponds to 16/15 mols. Fe per mol. CaSO_4 and for SrSO_4 about 8/9 mols. Fe per mol. SrSO_4 . The reaction with iron results in the formation of the well defined ferrites, $\text{Ca}_2\text{Fe}_2\text{O}_4$, $\text{Sr}_2\text{Fe}_2\text{O}_4$, BaFe_2O_4 . For CaSO_4 , with less than 16/15 mols. Fe, the residue after reaction contained the ferrite, CaSO_4 and CaS ; with 16/15 to 11/8 mols. Fe the residue was ferrite, CaS and FeS ; with 11/8 to 10/3 mols. Fe it was essentially ferrite, FeS and Fe_2O_3 ; if still more iron is present reduction occurs without formation of SO_2 .

J. A. ALMQUIST

Glimpse of the liquid carbon dioxide industry. A. G. WIKOFF. *Chem. Met. Eng.* 28, 5-9(1923).—Pure CO_2 is manufd. by burning coke under a boiler, absorbing the CO_2 in Na_2CO_3 solns., boiling the NaHCO_3 to liberate CO_2 , and compressing this into cylinders. A detailed flow sheet of the entire process including the by-products is given. The chief uses of the CO_2 are for carbonated beverages, the manuf. of Na_2CO_3 and NaHCO_3 , refrigeration plants, and many chem. products.

E. F. PERKINS

G. Fornì: a predecessor of E. Solvay. V. RAVIZZA. *Giorn. chim. ind. applicata* 4, 476-7(1922).—Historical and descriptive with sketch and outline of early Fornì method of soda manuf.

ROBERT S. POSMONTIER

Problems in sodium sulfide manufacture. B. T. ROCCA. *Chem. Met. Eng.* 28, 338(1923).—Niter cake, together with 20 to 30% gas-house C, is charged into an oil-fired reverberatory furnace. When 70% of the available Na_2SO_4 is converted the charge is tapped, cooled, ground and dissolved, the soln. is filtered and BaS is added until the SO_4 is pptd. The ppt. is washed and the *blanc fixe* sold. The Na_2S soln. is evapd., yielding an unusually pure Na_2S . Cf. *Chem. Met. Eng.* 28, 49(1923).

F. C. Z.

Refrigeration in the manufacture of sodium sulfate. FRANCESCO MAURO. *Giorn. chim. ind. applicata* 4, 453-6(1922).—Descriptive, with diagrams, of the process of mfg. Na_2SO_4 from a mixt. of $\text{MgSO}_4 + \text{NaCl}$, by the application of refrigeration.

ROBERT S. POSMONTIER

The production of barium salts from barytes. G. M. ADHIKARI, J. J. SUDBOROUGH AND H. E. WATSON. *J. Indian Inst. Sci.* 5, Part 7, 83-106(1922).—Details of and precautions in the reduction of barytes to BaS are given. BaCl_2 is obtained by heating BaS soln. with MgCl_2 soln. under pressure. An excess of MgCl_2 is not required and all S is evolved in one stage as H_2S instead of in a mixt. of SO_2 , H_2S and S.

W. H. BOYNTON

The Butters nitrate process. ANON. *Chem. Age* (London) 8, 90-1(1923).—The process consists of three steps: (1) sepu. of fines from coarse material by vibrating screens; (2) dissolution of the nitrate contents of the fines in agitation cooking tanks; (3) filtration of the pulp in Butters pressure filters. Each step is outlined and plant operation diagrammatically illus.

W. H. BOYNTON

Technical sedimentation analysis. II. F. V. v. HAHN AND D. v. HAHN. *Kolloid Z.* 31, 352-8(1922).—Detn. of the size of graphite particles for industrial purposes by passing the graphite through different sieves (meshes 1000 to 75) consumes much time and does not give the best results. The sedimentation method (C. A. 17, 246) gives better information of the technically important characteristics of the graphite particles and it is much more rapidly carried out.

A. MUTSCHLER

SCHERRO, MORRIS: Water Glass. A bibliography. Pittsburgh, Pa.: Carnegie Library. 83 pp.

- HOLTEDAHL, OLAF and ANDERSEN, OLAF: Om norske dolomiter med bemerkninger om dens praktiske anvendelse av dolomit. Kristiania: H. Aschehoug. 49 pp.
- WABER, BRUNO: Die Luftstickstoffindustrie, mit besonderer Berücksichtigung der Gewinnung von Ammoniak und Salpetersäure. Leipzig: Otto Spamer, 586 pp.

Hydrocyanic acid. W. G. DINGLE. U. S. 1,445,303, Feb. 13. Relatively pure HCN is obtained from crude cyanides contg. chlorides or other impurities by liberating HCN, together with some impurities, by the action of H_2SO_4 and then purifying the HCN by refrigeration and fractional liquefaction, during which less readily liquefiable substances are sepd. An app. is described.

Potassium sulfate. C. HORST. U. S. 1,446,185, Feb. 20. $CaSO_4$ suspended in an aq. soln. of KOH, is reacted on by CO_2 to form a satd. soln. of K_2SO_4 and the latter is sepd. from the soln. on cooling.

Cleansing silicon carbide. W. A. HARTY and F. W. MOORE. U. S. 1,445,943, Feb. 20. Si carbide is purified by agitating it successively with H_2SO_4 and H_2O , with or without additional treatment with an alk. soln.

Aluminium hydroxide sludge. C. W. SOUDER. U. S. 1,445,917, Feb. 20. A liquid sludge contg. coarse $Al(OH)_3$ is filtered relatively free from fine $Al(OH)_3$ by suction and the thickened sludge is subjected to continued suction filtration out of contact with the liquid sludge, to free it from liquid.

Zinc oxide. E. P. STREVENSON. U. S. 1,445,366, Feb. 13. Roasted Zn ore or a similar Zn-bearing material is treated with a hot concd. soln. of $(NH_4)_2SO_4$, the soln. is cooled to ppt. a basic Zn sulfate, the latter is treated with Na_2CO_3 (after NH_4 salts are driven off) and the ppt. thus formed is calcined to produce ZnO.

Nitrogen fixation. C. H. BUELTNER. U. S. 1,446,546, Feb. 27. Mixed N and O are fed together by convection through a flue and through a zone of substantially continuous elec. flaming arc interposed in the flue, to an absorption device for recovery of N compds. formed.

Sulfates of copper or other difficultly soluble metals. H. PAULING. U. S. 1,446,578, Feb. 27. Cu, Ni or similar substances difficultly sol. in H_2SO_4 are treated with HNO_3 to form a strongly acid nitrate soln., the latter is treated with H_2SO_4 and sulfate is crystd. from the soln., the crystals are sepd. and washed.

Rotary inclined horizontal kiln adapted for revivifying fuller's earth. F. PEYER. U. S. 1,446,857, Feb. 27. A drier drum discharges into a kiln drum and heating gases pass around the drier drum after heating the kiln drum.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Production of colorless glass in tank furnaces with particular reference to the use of selenium. I. A. COUSEN and W. E. S. TURNER. *J. Soc. Glass Tech.* 6, 168-81(1922).—Numerous small melts at 1380° and 1440° showed that not more than 0.09% of iron oxide in a glass could be effectively decolorized by Se or Na selenite. The greater corrosive action of the salt-cake on the pot and its action on the Se at high temps. rendered more decolorizer necessary for batches contg. this ingredient than for those with soda ash alone. Expts. showed the distinct formation of Na selenite from Se when dropped on to fused Na sulfate. In a batch contg. only soda ash and no salt-cake, Na selenite was much more effective than Se in decolorizing. Reheating the glasses only changed the tint of those which had been over decolorized, and then only when heated between 525° and 550° .

J. C. S.

The silvering of glass. *Optician* 60, 183(1920); *J. Soc. Glass Tech.* 5, 125.—Several methods are described. The first requires 4 solns., as follows: (1) 40 g. of crystd. AgNO_3 in one l. distd. water; (2) 6 g. of NH_4NO_3 in 100 g. of water; (3) 10 g. of KOH in 100 g. of water; (4) 25 g. of sugar in 250 g. of water; add 3 g. of tartaric acid, boil for ten min. and allow to cool, then add 50 cc. of alc. and dil. with water to 500 cc. All these solns. can be kept without undergoing alteration. Equal quantities of the 4 solns. are mixed and the glass is immersed in the mixt. with the side to be silvered facing downwards. The second method is a modification of Brashear's process. NH_3 is added to a 10% AgNO_3 soln. until the ppt. is re-dissolved; to the total vol. half as much of a soln. of KOH is added, and then more NH_3 until the mixt. is clear. A weak soln. of AgNO_3 is further added until a bright brown tint results. Silvering is carried out by using a mixt. of this and a sugar soln. contg. 10% of sugar, 10% of alc., and 0.5% of HNO_3 . The side of the glass to be silvered should be on top. For another method, two solns. are used: (a) 8.5 g. of AgNO_3 in 200 g. of water; (b) 15 g. of Rochelle salt in 200 g. of water. NH_3 is added to the mixt. until the ppt. is almost re-dissolved and the soln. filtered. Two solns. are also used in a fourth process: (1) sugar 20, HNO_3 4, alc. 175, water 1000 parts; (2) 15 cc. of a 1% AgNO_3 soln., 7.5 cc. of a 0.5% KOH soln., and 22 cc. of NH_3 . NH_3 is added to the AgNO_3 soln. until the ppt. is re-dissolved then the KOH soln., and finally the rest of the NH_3 . Soln. (1) improves with age; 170 cc. of it are added to soln. (2) as made. Looking-glasses can be silvered simply by employing a mixt. of a 1% AgNO_3 soln., which has been treated with NH_3 until the ppt. has nearly disappeared, and a 1% formalin soln. The surface to be silvered should be placed downwards. In all cases abs. cleanliness of the glass is essential and directions are given for ensuring this.

H. G.

Notes on reheating of glass electrically. E. F. COLLINS. *Glass Ind.* 3, 223(1922).—Glass is athermous to heat rays. At 100° 2.6 mm. of glass intercepts all heat radiotus and at 390° it intercepts all but 6%. The ratio of convected heat to radiated heat in the metallic resistor furnace varies from about 20% at 500° F. to about 3% at 1800° F. Hence in the electric metallic resistor furnace the reheating of glass at temps. required for molding is secured almost entirely by radiant heat, and the temp. is under perfect control.

J. B. PATCH

Leers. W. S. MAYERS. *Glass Ind.* 4, 21-3(1923).—The gas-heated leer requires only $1/4$ of the amt. of fuel consumption that the elec. leer requires.

J. B. PATCH

Study of chemical glass ware. T. OGAWA. *J. Japan. Cer. Assoc.* 355, 91-7; 358, 252-65(1922).—The results of chemical analyses and tests on the resistance to chemicals, impact and the sudden change in temp. of foreign and domestic chem. glass wares as well as those made by the author are given. In general, home products are inferior to foreign ones, because of their improper compns. Furnaces producing high temps. and pots standing them, are indispensable for making chem. glasses of the best quality, since the constituents of glass which increase its resistance to chemicals make it more refractory. Batches contg. proper proportions of ZnO , Al_2O_3 , MgO , B_2O_3 and SiO_2 are suitable for furnaces with half gas firing. The use of sands contg. Al_2O_3 , feldspar, or dolomite is economical.

S. KONDO

The heat balance of glass leers. G. GIANOLI. *Ind. laterizi ed aff.* 1, 16-8(1922); *Chimie et industrie* 9, 115(1923).—G. counts on the following losses: producing steam required by the gas producer 3-3.2%; in gas producer (unburnt fuel in ashes, soot, radiation) 1.2-1.5%; cooling of the gases in the ducts 4-4.1%; regenerating chambers 6.1-6.7%; conduction and radiation from the leer 43-44.9%; flue gases 19%. There remains but 12.5-13.7% for the fusion of the glass.

A. P.-C.

Making glass for Ford windshields. F. J. HUNTLEY. *Glass Ind.* 4, 1-4(1923); 6 illus.—Historical and descriptive of the glass factory being built near Detroit. It will comprise 4 furnaces.

J. B. PATCH

Burnt lime or limestone. I. E. ADAMS. *Glass Ind.* 4, 6(1923).—There is no discernible trend away from a burnt lime basis in glass hatches in those fields where it has become standard practice.

J. B. PATCH
Opportunity for an American glass training school. WM. M. CLARK. *Glass Ind.* 4, 9(1923).—A discussion of the Glass Trade School in Zwiesel, Bavaria. Cf. C. A. 5, 1327.

J. B. PATCH
The making of watch crystals. W. H. HOLMES. *Glass Ind.* 4, 25-8(1923); 6 illus.—A brief story of the building up of this industry in America by the Waterbury Clock Co.

J. B. PATCH
Resistivity of vitreous materials. L. L. HOLLADAY. *J. Franklin Inst.* 195, 229-35 (1923).—A study of the resistivity of hard, light flint, and lime glasses. J. S. H.

J. S. H.
Refractories for air furnaces. C. E. BALES. *Foundry* 51, 112-7(1923).—Firebrick manufacturing is described. "The longer firebricks are burned the poorer their quality" because Fe compds., exposed to a smoky flame, are reduced to the ferrous condition forming fusible, silicate slag. Longer burning also gives greater d. and consequently less resistance to spalling. Bricks for hungs or roofs should contain at least 38% Al_2O_3 and be coarse grained, open textured and soft burned. Side wall brick should be refractory but fine grained, close textured and hard burned. Some analyses and data are given.

C. H. KERR

Electric enameling furnace (ANON) 4.

CREMER, FERDINAND: Die Fabrikation der Silber-und Quecksilber-Spiegel od das Belegen der Spiegel auf chemischem und mechanischem Wege. 3rd revised ed. Vienna and Leipzig: A. Hartleben. 224 pp.

Polishing rouge. P. J. HESS. U. S. 1,446,181, Feb. 20. A mixt. adapted for polishing plate glass is formed of basic ferric sulfate 1 and Fe_2O_3 2 parts mixed with H_2O in the proportions of 1 lb. to 4.5 gals.

China clay. N. TESTRUP. U. S. 1,446,949, Feb. 27. Wet china clay contg. a large amt. of liquid is freed from superfluous liquid until a layer is obtained of small av. liquid content, varying through the layer, and clay is removed from the denser portion of the layer and fed as a film on to a drying surface heated by compressed vapor to a temp. only slightly in excess of that necessary to evap. the moisture in the clay.

Brick. G. TUMURA. U. S. 1,446,238, Feb. 20. Crushed grains of liparite 1 and clay 3 parts are used together to form a brick which is light and fire-resistant.

20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WITT

Magnesium oxychloride cements. M. Y. SEAYON. *Chem. Age* (N. Y.) 31, 17-22 (1923).—Mg oxychloride cement was originally made by Sorel in 1867. It is important as a binding material because it attains high strength at an early age even with free exposure to air. It does not exhibit a high vol. change due to temp. changes or other causes. The raw materials, manuf. process, selection of suitable aggregates, and the use of oxychloride cements are discussed.

J. C. WITT

Mineral aggregate specifications for asphalt pavements. R. M. GREEN. *Rock Products* 25, No. 10, 34-6(1922).—Specifications for the amt. and grading of aggregates are given for each of 4 classes of asphalt paving mixts.: (1) sheet asphalt wearing surface mixts., (2) asphaltic concrete, with the material passing the 10-mesh sieve predominating, (3) asphaltic concrete, with substantial proportions both passing and retained

on the 10-mesh sieve, (4) asphaltic concrete, with a preponderance of material retained on the 10-mesh sieve. Standards for the requirements of the physical properties of aggregates should not be so rigid as to eliminate local materials of merit. They should be based on the materials available in any locality and should be so drawn as to admit all aggregates that have proved successful and exclude all materials that have proved inferior in the past.

J. C. WITT

The viscosity of raw material slurry used in the manufacture of portland cement.

J. W. CRISTELOW AND E. BOWES. The British Cement Research Assoc., *Pamphlet No. 2* (1922).—It has been known for many years that small quantities of certain substances, particularly Na_2CO_3 , reduce the viscosity of mixts. of clay and water. The object of this investigation was to det. the effect of such substances on the viscosity of slurry and to devise a lab. method suitable for use in cement plants. Most of the work was carried out with Na_2CO_3 but other Na and Ba compds. were tried out also. The effects of time of storage, temp., elec. current and sol. compds. originally present in the slurry were studied. Viscosities were detd. by the use of a viscosimeter consisting of an inverted glass bottle (from which the bottom had been removed) fitted with a cork through which passed a glass tube $\frac{5}{16}$ in. in diam. and $2\frac{1}{4}$ in. long. Both ends were rounded and the upper end of the tube was flush with the cork. The viscosimeter was filled with slurry to a given mark and the time necessary for 250 cc. to flow from the app. noted with a stop watch. Readings were made in triplicate on samples that had reached room temp. No stirrer was found necessary. The viscosity was expressed either in seconds or in water units (which equals the time in sec. for a slurry divided by the time required for water, that is, 4.3 seconds). Preliminary results showed that the most advantageous amt. of Na_2CO_3 to use is 0.075%. Eighteen samples of slurry from 11 plants treated with this amt. showed decreases in viscosity equiv. to 0.6% to 4.6% H_2O . For example, a slurry contg. 40% H_2O had the same viscosity after the addition of 0.075% Na_2CO_3 and a decrease in the H_2O content to 36%. Data showing the increase in economy of operation of a plant as a result of decreasing the H_2O content of slurry are given.

J. C. WITT

Quality control in cement manufacture. R. K. MEADE. *Chem. Met. Eng.* 27, 250-3 (1923).—The qualities most desirable in cement are soundness, strength, and uniformity in the rate of setting and hardening. All are dependent to a marked degree on chem. compn., the fineness of the raw materials, and the burning. These factors are, therefore, the ones which must be under perfect control. Of these, the chem. compn. is the most important. Perfect control of the chem. compn. of raw mix enables a plant to produce cement strong and uniform in setting and hardening qualities.

J. C. WITT

Plant transportation, plant roadways, and concrete. G. L. MONTGOMERY. *Chem. Met. Eng.* 26, 1169-70 (1922).—The use of concrete for plant roadways is recommended.

J. C. WITT

Effect of hydrated lime on the strength and flow of concrete. W. E. EMLEY. *Proc. Am. Soc. Testing Materials* 22, Pt. I, 284-7 (1922).—At the Bureau of Standards 1600 specimens of concrete with and without lime and with varying amts. of water and different storage conditions were tested for compressive strength and flow. Conclusions: (1) If water, but no lime, is added to a given concrete, the flow will be increased and the strength decreased. (2) If lime, but no water, is added to a given concrete, the flow will be decreased and the strength increased. If both lime and water are added to a given concrete, the effect on both the strength and the flow may be plus, minus, or zero, depending on the numerical values of the factors involved. These factors are the character of the given concrete: the change due to the lime, and the change due to the water.

J. C. WITT

Effect of hydrated lime on the strength and flow of concrete. H. C. BERRY. *Proc. Am. Soc. Testing Materials* 22, Pt. I, 290-307 (1922).—The effect of 0.5% and 10% of

lime (on the basis of the cement) on the compressive strength of 6 by 12-in. concrete cylinders was detd. In making the specimens, the flow was kept const. but because of the condition of the lime the water percentage had to be varied; hence, it was not conclusively shown whether the lime increased or decreased the strength, though in 6 of 8 cases there was a greater strength in the specimens contg. lime. The general conclusion is that the condition of lime had no harmful effect on the strength of concrete.

J. C. WIRR

Analysis of tests on effect of hydrated lime in concrete made at Lewis Institute. T. B. SHERTZER. *Proc. Am. Soc. Testing Materials* 22, Pt. I, 269-83(1922).—A discussion of a paper by Abrams on the effect of hydrated lime and other powdered admixtures on concrete. Failure to take into account the fact that the properties of hydrated lime differ from those of portland cement has led to a misinterpretation of results, and the erroneous statement that hydrated lime decreases the strength of concrete.

J. C. WIRR

Relations between voids and plasticity of cement mortars at different relative water contents. F. E. RICHART AND E. E. BAUER. *Proc. Am. Soc. Testing Materials* 22, Pt. II, 385-403(1922).—A method of detg. voids and the effect of voids on the strength of concrete are discussed. (1) When a mixt. of dry sand and cement is gaged with increasing amts. of water there occurs at first a swelling of bulking of the mass much as is produced in sand alone when dampened; (2) this is followed by a gradual decrease in the vol. as the mixture develops cohesive properties until a point of minimum vol. is reached, where the mortar begins to become plastic; and (3) with more water an increase in the vol. is caused by the mechanical sepn. of the particles, or diln. of the mixt., by the additional water.

J. C. WIRR

Physical properties of subgrade materials. J. R. BOYD. *Proc. Am. Soc. Testing Materials* 22, Pt. I, 337-61(1922).—The following tests are described: mechanical analysis, water-holding capacity, moisture equivalent, vertical capillarity, volumetric change, comparative bearing value, slaking value. The terms sand, silt, clay, suspension clay, mechanical ratio, percentage of voids, and moisture index are defined. Complete analysis of 57 subgrade soils is given.

J. C. WIRR

Fatigue of concrete. H. F. CLEMMER. *Proc. Am. Soc. Testing Materials* 22, Pt. II, 408-19(1922).—Research carried on by the Ill. Div. of Highways indicates that: (1) concrete beams will fail under a number of repetitions of loads which produce stress equal to or greater than a certain percentage of that required to cause transverse failure when tested under one application of load; (2) loads which produce stress less than a certain percentage of the modulus of rupture as detd. in the testing machine will not cause failure on repetitions, but rather, as indicated in the first and fourth series, the strength of the specimen would actually be increased by this condition of load if the load is near this critical percentage; (3) the critical percentage or limit of endurance of the concrete specimens was between 51 and 54% of the modulus of rupture as detd. from one application of load; (4) for the same percentage of ultimate strength, a considerably less number of applications of load is required to cause failure in the 1 : 3 : 5 mix specimens than in the 1 : 2 : 3 1/4 mix specimens; (5) stresses below the limit of endurance do not cause permanent deformation in the specimen; (6) for stresses beyond the limit of endurance, the number of repetitions of load required to produce failure decrease with increase of percentage of stress.

J. C. WIRR

Investigation of effect of hydrated lime in concrete. H. F. CLEMMER. *Proc. Am. Soc. Testing Materials* 22, Pt. I, 288-9(1922).—Results so far obtained indicate that hydrated lime does not increase the transverse strength of concrete. The presence of 5% of hydrated lime in specimens made with coarse sand increases the compressive strength to some extent. In specimens contg. fine sand, however, hydrated lime appears to decrease the compressive strength.

J. C. WIRR

Gypsum plaster and wall boards. J. M. PORTER. *Proc. Am. Soc. Testing Materials* 22, Pt. I, 358-63(1922).—The breaking load and the modulus of rupture of 31 specimens of plaster boards and wall boards are given. J. C. WYRR

Technology of slate. OLIVER BOWLES. *Bur. of Mines, Bull.* 218, 128 pp.(1922).—The purpose is to enable the slate quarryman to reduce his production cost, to improve the quality, and increase the variety of his products that he may compete more favorably with producers of substitute materials. A study of slate quarrying was begun in 1920. Sixty-five quarries were visited and a detailed study was made of their operation. The bulletin discusses the origin of slate, its mineralogical and chem. compn., and its phys. properties. Methods of quarrying, particularly in relation to increased economy, are taken up in detail. Proposed methods of utilization of waste slate include its use as fillers for rubber, linoleum, oilcloth, plastic roofing and flooring, and asphalt mixts.; in ceramics; and in a number of miscellaneous ways. J. C. WYRR

Preservation of stone. NOEL HIRATON. *J. Roy. Soc. Arts* 70, 123-39(1921).—New stone work can be rendered more resistant to decay by treatment with fluosilicates. Faulty or face-bedded stones cannot be effectively preserved. Decayed stones can be preserved for a limited period by treating with soft soap and alum. $\text{Ba}(\text{OH})_2$ is, in many cases, beneficial to stones which have been corroded by S compds. Preservative treatment should be employed only where it is certain it will do no harm. Construction details, such as the prevention of damp, and the carrying away of storm water reduce decay and are more important than preservative treatment. J. C. WYRR

BUB-BODMAR, F. and TILGER, B.: *Die Konservierung des Holzes in Theorie und Praxis*. Berlin: P. Parey. 1006 pp.

Road pavement. J. S. ROBESON. U. S. 1,445,240, Feb. 13. A road pavement is formed with mineral aggregate including blast furnace slag or other silicates which are attacked by HCl and sulfite waste liquor, treated with the latter and MgSO_4 .

Hardening articles of cement and concrete. O. ROUCKA. U. S. 1,446,213, Feb. 20. Raw articles of cement or reinforced concrete are heated in a closed vessel at the rate of $1-5^\circ$ per min. to a temp. of about $60-80^\circ$ and then further heated at the rate of $0.1-1^\circ$ per min. while increasing the pressure to about 7-13 atm. and the articles are maintained under this pressure for about 8-10 hrs.

Gypsum-calcining apparatus. S. E. and F. F. TOWNLEY. U. S. 1,446,863, Feb. 27. The app. comprises a fire-box and superposed flue-housing in which is mounted a multi-compartment "kettle-shell" with flues passing through and around its superposed compartments.

Wall-board composition. W. DUNSTAN. U. S. 1,445,204, Feb. 13. Wall-board sheets are formed with a body portion of clay, chalk, marl or clay slimes, hemp or other long vegetable fiber, Na silicate, CaCl_2 and Fe oxide, with an outer cement coating and an inner coating of plaster of Paris.

21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

The terminology of liquid fuels. F. BORDAS. *Ann. fals.* 16, 6-16(1923).—An outline of the almost inextricable confusion existing in various countries as regards the terminology, properties and methods of testing liquid fuels, and more especially petroleum products. At the Congress of Liquid Fuels (Paris, Oct. 1922) it was practically unanimously acknowledged that international unification of methods of analysis was impossible. A "preliminary inventory" of the terminology in the various countries

is to be made in the resp. countries. It is to be followed by an exhaustive comparison of different methods of analysis. A. P.-C.

Combustion of powdered coal. H. KREISINGER AND J. BLIZARD. *Ind. Eng. Chem.* 15, 249-51(1923).—The size of coal particles passing a 200-mesh sieve varied from 2 to 60 μ ; most of them had mean diams. between 20 and 60 μ . The effect of air and furnace gases on the velocity of these particles is discussed; Audibert's values for densities are used: of coke 1.9, anthracite 1.5, and bituminous 1.3. The method of burning powdered coal in a recently installed plant is described. The flame in the furnace was U-shaped. The paths of the different sized particles of coal, together with conditions for their attaining equil. velocity, are discussed and illustrated with a cross-section diagram of the installation. The results of boiler tests at this plant are summarized graphically by 6 curves, which show that the biggest economical rate of heat evolution for this furnace was 23,000 B. t. u. per cu. ft. of effective combustion space and that properly sized coal can be burned nearly completely with 10 to 25% of excess air. The thermal efficiency of boiler and superheater was above 80% and including the economizer reached 90%, which is about the highest efficiency so far attained on a large power-plant steam-generating unit. W. W. HODGE

Air regulator for (boiler) firing. ANON. *Z. angew. Chem.* 36, 55-6(1923).—A description, without cut, of the Liese regulator which controls the stack draft according to the resistance of the fire bed by means of a bell float in a H₂O seal. J. H. MOORE

Contribution to the theory of the water-gas process. J. W. TERWEN. *Chem. Weekblad* 19, 400-1(1922).—Among some errors in the work of Kohn (*C. A.* 16, 634) the chief is the assertion that in the two equations, $C + 2H_2O = CO_2 + 2H_2$ and $CO_2 + C = 2CO$, the fraction of steam, transformed according to the first equation, should be equal to the quantity of CO₂ which disappears according to the second equation. R. B.

The "blowing off" of the flame of a Bunsen burner. KARL GLASER. *Z. angew. Chem.* 36, 38(1923); cf. BRONN, *C. A.* 17, 332.—The tendency of the Bunsen flame to leave the burner is not peculiar to CH₄, but occurs with all gases when the supply pressure is raised so that the velocity of flame propagation is less than that of efflux. ERNEST W. THIELE

Distillation of combustibles at low temperatures and the primary tar. CARLO PADOVANI. *Giorn. chim. ind. applicata* 4, 466-75(1922).—Monograph, with photograph, statistical diagrams and sketches of app. used. The topics are: general procedure of distn. at low temp. and its relation to coking at elevated temp.; utilization of products of low-temp. distn., (a) primary tar, (b) sepn. of tar into its components and their sep. washing; by-products (a) semicoke, (b) gas, (c) ammoniacal liquors and nitrogen; app. for low-temp. distn. ROBERT S. POSMONTIER

Germans distil tar from coal while burning under boiler. ALFRED GRADENWITZ. *Power* 55, 970(1922).—A new type of combined furnace and distn. plant is described and illustrated. As the coal passed through a shaft on to the grate it is subjected to partial distn. The gases given off are freed from tar, NH₃, etc., and returned to the furnace. The dry tar obtained varied from 2.25 to 5.53% of the fuel. D. B. DILL

By-product coking during the past year. C. J. RAMSBURG. *Blast Furnace Steel Plant* 11, 18-9(1923). E. J. C.

By-product coke-oven operation. "10" pushing series. A. COR. *Blast Furnace Steel Plant* 10, 619-22(1922).—Diagrammatical illustrations are given of the various "10" series also of the "11" series. C. endeavors to prove that the "G" is the best "10" pushing series obtainable, as it gives the most uniform product, likewise approaches theoretical correctness as regards heat distribution. C. T. WHITE

Combustion of blast-furnace cokes in fuel beds. R. A. SHERMAN AND J. BLIZARD. *Trans. Am. Inst. Mining Met. Eng.* No. 1217-S, 17 pp.(1923).—The results of tests

made to det. the relative combustibility of 4 kinds of blast-furnace coke, also the analyses and phys. properties of the cokes, are given in tabular form. The description of the methods used is illustrated with a cross-section diagram of the exptl. furnace. The discussion of results is elucidated by 5 sets of curves showing: compn. of stack gases and temps. from various cokes at varying rates of combustion; the varying O_2 and CO content of gases and temps. at different levels in the fuel bed; av. compn. of gases and temps. in fuel beds; mean O_2 and CO content of gases and temps. in fuel beds of different fuels; and the mean combustibility of the 4 cokes, and of 4 other fuels tested by the Bureau of Mines (*C. A.* 11, 1740 and 13, 1379). The expression $(CO_2 + CO/2CO_2 + CO + 2O_2) \times 100$ is taken as giving an approx. measure of the mean combustibility expressed as a percentage of the max. obtainable. S. and B. conclude that: the rate of combustion, within wide limits, has no great effect on the final products of combustion; the relative mean combustibilities of the 4 cokes are different in different parts of the fuel bed; for the entire fuel bed calcd. from the stack gases, the mean combustibilities of the different cokes when burned at approx. 25 lbs. per sq. ft. per hr. varied from 73% to 77%. W. W. HODGE

A new method for determining the hardness of coke by abrasion. A. SCHMOLKE. *Glückauf* 59, 3-6(1923).—The hardness of coke is detd. by grinding on an emery wheel. Samples are prepd. of such a shape that the surface abraded remains const., and the pressure is kept const. by a lever beam with wts. holding the sample against the wheel. The abrasion is measured in terms of the loss in wt. per revolution. The app. is described and illustrated, and results for 20 cokes are given. C. C. DAVIS

Thermal operation of modern regenerator coke ovens. D. W. WILSON, H. O. FORREST and C. H. HERTY, JR. *Ind. Eng. Chem.* 15, 251-4(1923).—A heat balance on a 60-oven battery of regenerator ovens showed a thermal efficiency of 87.38%. From the data obtained the coking reaction was found to be exothermic to the extent of 452 B. t. u. per lb. of dry coal charged. C. H. HERTY, JR.

The Springfield gas explosion (WEDGER) 24. Fuel gas question in the steel industry (DENK) 9.

LESLIE, EUGENE H.: *Motor Fuels—Their Production and Technology*. New York: The Chemical Catalog Co., Inc. 600 pp. \$7.

Sampling and Analysis of Coal, Coke and By-products. Methods of the Chemists of the U. S. Steel Corporation. Pittsburgh: Carnegie Steel Co., Bureau of Instruction. 184 pp. \$3. Reviewed in *Chem. Met. Eng.* 28, 223(1923).

Liquid hydrocarbons from peat. T. ULKE. U. S. 1,445,423, Feb. 13. Peat is hydrogenated with Na formate under a pressure of about 100 atm. at a temp. of about 400°. NaOH in solid form and CO are obtained from the products and are used to regenerate Na formate for treating a new charge of peat. The liquid hydrogenation products formed from the peat are sepd. Oil shale, lignite, coal and sawdust may be similarly treated.

Lignite fuel briquet. G. F. SHEEHAN and H. A. GILLEN. U. S. 1,446,322, Feb. 20. A vulcanized binder formed of bitumen 4 and S 1 part is used with lignite in forming briquets.

Gas producer. R. DAAR. U. S. 1,445,300, Feb. 13. The pat. relates to a mechanism for supplying fuel to a producer through a feed opening in the cover.

Pure cresol from crude tar acids. I. H. DERBY and W. HIGBURN. U. S. 1,445,668, Feb. 20. Crude-tar acids are treated with a small fraction of the chem. equiv. amt. of caustic alkali and after reaction the material is cooled, C_6H_6 or toluene is added and the material is extd. with H_2O to sep. the alkali metal compds.

Coking blended fuels. S. R. ILLINGWORTH. U. S. 1,445,954, Feb. 20. See Brit. 186,085 (C. A. 17, 336).

Coke from high-volatile coal. J. G. WEST. U. S. 1,445,735, Feb. 20. Metallurgical coke is formed from high-volatile coal by distn. to reduce the volatile contents to 6% or somewhat more, cooling the residue, mixing it with at least an equal amt. of raw coal and coking the mixt.

Utilizing waste heat from coke. O. BRENDL. U. S. 1,446,960, Feb. 27. Heat from coke is recovered or regenerated by passing inert gas, *e. g.*, CO₂, N or flue gas, in contact with the hot coke, dividing the current into zones of diff. temp. and conveying the gas of each zone separately to a heat-consuming device, *e. g.*, a steam boiler.

Regenerative horizontal coke oven with vertical heating flues. O. PRIETZ. U. S. 1,445,552, Feb. 13.

22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Resolution of petroleum emulsions. H. V. DODD. *Chem. Met. Eng.* 28, 249-53 (1923).—The essential property of an emulsifying agent is its ability to form a coherent film at the interface of the liquid phases. Lowering of the interfacial tension favors emulsification, but is not an essential factor. Complex hydrocarbons, such as asphalt and asphaltenes, present in the proper degree of dispersion are the emulsifying agents in oil-field emulsions. The presence of low-boiling fractions insures the proper degree of dispersion for emulsification. In all cases examd., addn. of gasoline made the breaking of emulsions more difficult. Emulsions were made by placing 50 cc. of distd. H₂O and 100 cc. of asphaltum cement dild. with varying proportions of gasoline, into a graduated 500-cc. cylinder. Mixing was effected in 2 min. by revolving a 1.5-in. turbine stirrer, at a speed of 3500 r. p. m. Low percents of asphaltum (0.05) gave no emulsions. Twenty cc. of H₂O was emulsified by a 0.1% solu., and all of the H₂O by solns. more concd. than 0.2%. From the excess of gasoline, the emulsions sepd. quickly as compact brown masses. Similar emulsions were obtained from an oil-field emulsion by dild. with gasoline and centrifuging. The order of efficiency of acids in breaking an emulsion from the Midway-Sunset (Cal.) field was the reverse of that found by Sherrick for a Goose Creek (Tex.) emulsion (C. A. 14, 833). Other electrolytes in aq. soln. did not break this emulsion satisfactorily. The effect of substances sol. in oil and differing in soly. in H₂O was investigated. In each test, 2 cc. of the substance was added to 20 cc. of the emulsion in a centrifuge cup. The H₂O content of the emulsion was 25.6%. After heating to 45°, the mixt. was shaken for 1 min., by hand, and then kept at this temp. for 3 hrs. The % of H₂O sepd. by centrifuging for 5 min. (conditions not given) was detd. There is no close parallelism between efficiency and soly. in H₂O, but the best substances were appreciably sol. in both oil and H₂O. Acetic acid in fusel oil is more effective than either substance alone. Phenol was the best substance found, when used in conjunction with enough acid to neutralize the alkalies of the emulsified H₂O. Kerosene acid sludge may be used as the source of H₂SO₄. Application of some heat is necessary. The effect of acid remaining in the oil, on pipe-lines, refinery equipment, etc., is undetd.

W. F. FARAGHER

Expansion of petroleum oils. J. B. RATHBUN. *Petroleum Age* 11, No. 5, 37 (1923).—The true vol. of a petroleum oil is found for temps. above 60° F. by the formula $V = \text{vol. at temp. read} / [(\text{temp. read} - 60^\circ \text{F.})K] + 1.00$ and for temps. below 60° F. by the formula $V = [(\text{temp. read} - 60^\circ \text{F.})K + 1.00] \times \text{vol. at temp. read}$. K is a coeff. of expansion for petroleum oils obtained from the tables given which cover oils from 10 to 90° Bé. gravity.

D. F. BROWN

The use of Hanus's method for the determination of the iodine figure of mineral oils. JAN HLADKY. *Chem. Listy* 16, 207-11(1922).—The method of Hanus, whereby the I figure of mineral oils and bitumens is detd. by means of a soln. of I bromide in CCl_4 , is examd. It is found that the reagent does not depreciate as rapidly as those used in the methods of Hübl and of Wijs (B. Gracie, *Petroleum* 12, 631(1905)) and that the difference produced in the I figure by increasing the time allowed for reaction is smaller than for the above methods. The concn. of the reagent and the reaction temp. are not of great importance, while it is essential that the quantity of oil used is such as to leave a large excess of reagent after interaction. The presence of small quantities of water does not appear to affect the reaction. A further advantage of this method is that it permits the use of CCl_4 , a universal solvent for the bitumens. The accuracy attainable is, for oils of a low I figure, from 1 to 2 units. J. C. S.

Miscibility of hydrocarbons and liquid sulfur dioxide. F. FONTEIN. *Z. angew. Chem.* 36, 4-6(1923).—The limited soly. of PbCH_3 and of tetralin in liquid SO_2 observed by Zerner, Weisz and Opalski (*C. A.* 17, 1324) is attributable to the presence of H_2O in the systems examd. by them. Dry SO_2 and each of the two hydrocarbons remain homogeneous at temps. as low as -21° . At temps. below 10° , crystals of $\text{SO}_2 \cdot 6\text{H}_2\text{O}$ cause a turbidity, and suggest sepn. of a second layer. However, the relative masses of the two layers are not at all what the binary curve of Z., W., and O. would require. The approx. m. p. and sp. gr. of the crystals, as detd. by F. in some mixts. of the compn. used by Z., W., and O., prove that the hydrate was present in their systems. F. questions the limited soly. of SO_2 and naphthalene, castor oil or linseed oil, but he has made no investigation of these systems. W. F. FARAGHER

Miscibility of hydrocarbons and liquid sulfur dioxide. E. ZERNER, H. WEISZ, AND H. OPALSKI. *Z. angew. Chem.* 36, 6(1923).—The conclusions of Fontein (above) relative to PbCH_3 and tetralin are accepted. Of the other three systems, only one, castor oil and liquid SO_2 , is completely miscible at the temp. of a mixt. of ice and salt. W. F. FARAGHER

Kerosene, its manufacture. *Petroleum Age* 11, No. 4, 15-6, 66(1923).—Aromatic hydrocarbons or asphaltic substances are undesirable in kerosene. In treating it is essential to wash thoroughly, after the caustic treatment, to remove completely any Ca or Mg soaps which may have been formed. High-boiling fractions in kerosene lower its illuminating value. Too many light ends should be avoided, because they are needed to meet the gasoline requirements; they give the product too low a flash point; and they cause greater consumption in burning the product. Too many heavy ends must be avoided, because the resulting product will have too high a viscosity, excessive incrustation of the wick, and cause excessive smoking of the lamp. Excess S is apt to be associated with heavy ends. It is essential that as good fractionation as possible be obtained in the distn. of the crude. D. F. BROWN

Vapor-tight tank to check evaporation losses. L. SCHMIDT. *Nat. Petroleum News* 15, No. 7, 43-8(1923).—To obtain the greatest return from vapor-tight equipment the operator should expect to give the app. constant care and attention. Evapn. losses, which may take place in vapor-tight tanks because of faulty condition or operation of the valves, are such that they cannot be readily observed. Leaks in the tankage and equipment may develop and the possible savings of the investment may be lost without the knowledge of the operator, unless he conducts regular exams. and inspections. Six field tests on evapn. losses showed

| | % evapd. | Daily av. bbls. | Drop in gravity. |
|------------------------------------|----------|-----------------|------------------|
| Original equipment, open-top tanks | 4.44 | 12.33 | 1.7° Bé. |
| Gas-tight equipment | .58 | 1.55 | 0.25° Bé. |

The tests were made with 35° Bé. Mid-Continent crude oil in the months of June and July. D. F. BAOWN

The hypochlorite method of oil refining. ANON. *Petroleum Times* 9, 211-2 (1923).—The hypochlorite soln. is best prepd. fresh by means of liquid Cl. The S derivs. in the petroleum distillates are quickly oxidized. A concn. of 12 to 15 g. of available Cl per l. is employed and agitation is accomplished by circulating the aq. soln. through centrifugal pumps discharging below the surface of the oil. It is best to refine the crude naphtha distillate, steam distil off the gasoline and filter the kerosene residue through dhydrated hauxite. With Persian oil the combined losses by this method amounted to about 0.5% as compared with about 3% for the usual acid treatment. A oucc run naphtha contg. 0.15% S treated as above showed 0.01% S and a like amt. of Cl in the gasoline and the kerosene after filtration was water white and had a S content of 0.06 to 0.1% and 0.01% Cl.

D. F. BROWN

Absorption process gains favor in Oklahoma. G. TRIPLETT. *Refr. and Nat. Gasoline Mfr.* 1, No. 4, 9-11 (1922).—97% recovery is possible by the absorption process, as compared with 80% by the compression process.

D. F. BROWN

Society's research sheds new light on the fuel problem. V. H. GOTTSCHALK. *J. Soc. Automotive Eng.* 12, 3-9, 211-2 (1923).—Four straight-run gasolines having practically the same 10% points but varying in end point from 400° to 500° F. were tested in 55 automobiles covering a total mileage of 54,259 mi. The mileage per gal. did not vary more than 2.6% for summer driving. The two fuels having the lowest end point gave the best satisfaction but difficulty was experienced with the highest end point. Crank case diin. increases progressively with decreasing volatility and the rate of increase is more marked for the heavier fuels.

D. F. BROWN

Economic motor fuel volatility. R. F. CARLSON. *J. Soc. Automotive Eng.* 12, 138-50 (1923).—Description of the Bur. of Standard tests on 4 grades of motor gasoline. Tests were conducted and results obtained similar to those reported by the research committee of the S.A.E. (cf. preceding abstr.).

D. F. BROWN

The oilfields of Saghalin. B. BEHAGHEL. *Oil Eng. & Finance* 3, 149-52, 165-6 (1923).—A general description covering the geology and topography of the region. The oil zone is about 240 miles long and great masses of oil appear on the surface, much of it as asphalt. The oil yields about 0.4-0.5% of benzine and 34-44% of kerosene.

D. F. BROWN

Oil shales of the United States. D. T. DAY. *Oil Eng. & Finance* 3, 209-15 (1923).—A general survey of the industry.

D. F. BROWN

Oil from South African shale. ANON. *Petroleum Times* 9, 251 (1923).—The Lamplough-Harper process of shale distn. yields a distillate contg. no permanent gases. The crushed shale is fed into a vertical retort through a hopper and does not come into contact directly with the fire-heated surfaces of the retort. The oils extd. are said to be very clean and sweet; they are thoroughly steam scrubbed while in the vaporous condition, by which their quality is greatly improved. From the retorts the vapors pass into a fractionating and scrubbing tower where the crude oil is sepd. into a light fraction, lubricating oils, gear and axle greases, wax and a bituminous residue suitable for road construction. The lighter fractions (b. 60-300°) rise into the upper part of the tower and thence into a special app. in which motor spirit, kerosene and a substitute for paint oil are formed. A yield of 49.4 gallons of crude oil per ton of shale was obtained yielding 40.34% of motor spirit.

D. F. BROWN

The invasion of water into sands wet by oil. O. W. SHERWIN. *Petroleum Times* 9, 160 (1923).—Fine sand averaging 0.2221 mm. diam. per grain was put on top and bottom of a series of layers in a glass vessel, the center being occupied by a relatively coarse sand. After satn. of the sand with oil a hrine soln. of 1.1 sp. gr. was made to invade the sands. Various combinations of sand and 3 grades of oil of different viscosity were used. In each case the water entered the coarse-grained sand more readily than the

fine regardless of the porosities of the sands. With high-viscosity oil the pressure used (1.4 ft. of water) was sufficient to force the oil out of even the coarse sand. Capillary tubes wetted with oil and immersed in water showed no rise of water above the water level outside, but tubes wetted with water and immersed in oil showed a normal rise of oil. Applications of these data to the problem of obtaining oil from oil sands are discussed.

D. F. BROWN

The origin of oil and gas. E. S. PERRY. *Petroleum Age* 11, No. 5, 17-8(1923).—A general article on the origin of petroleum and the geological reasons for the location of deposits.

D. F. BROWN

Prospecting and testing for oil and gas. R. E. COLLOM. *Bur. of Mines, Bull.* 201, 164 pp.(1922).—The surface evidence of oil and gas derived from out-croppings has to be supplemented by data obtained from drilling in order correctly to det. the geologic and structural relations of oil- and gas-bearing strata. In drilling, the various strata penetrated are of decided value and are classified as reservoir, barrier, marker, and indicator rocks. Reservoir rocks are all formations that may be reservoirs for fluids. Such formations are usually sedimentary rocks, limestone, sandstone, or shale. The barrier rock, which is usually slate, quartzite, or silicified shale, acts as an impervious envelope or seal for the oil or gas. An impervious stratum is a warning of oil or gas since a reservoir is always covered by such a stratum; such a barrier formation is necessary to shut out water and to prevent the migration of oil and gas to porous barren strata. Marker rocks are those reservoir and barrier rocks that because of their persistence and uniformity in texture, color, and content are easily identified as marker or key beds. Indicator rocks are those rocks, gases, or minerals that may be or are considered indicators of oil, such as natural gas, CH_4 , H_2S , CO_2 , NH_3 , oil, tar, and asphaltum, NaCl deposits, coal, S, and large amts. of H_2O . The sampling and identifying of cuttings from the drill are considered in detail from the following points: record sheet, color, chem. compn., and such physical tests as hardness, acid, lume, and fire tests, contamination, and preservation of the sample. The three fundamental principles of testing for oil, gas and water are: (1) no reservoir can be properly tested for fluid until all fluid from extraneous sources has been excluded; (2) the content cannot be detd. from the appearance of a sand or other reservoir rock; (3) all porous strata penetrated by the drill will either give up or absorb fluids.

E. F. PERKINS

A convenient and reliable retort for assaying oil shales for oil yield. L. C. KERRICK. *Bur. Mines, Repts. Investigations* No. 2229, 6 pp.(1921).—A retort for the detn. of oil yield from oil shales has been developed which is convenient and accurate for rapid assays in the field or lab. and gives an agreement between duplicates of 2% in volumetric detns. and 1% in gravimetric. The amt. of oil by this method minus 2 gals. per ton is the quantity that will be obtained under careful operation with the Scotch lab. assay retort. Details of operating the retort, measuring the oil and calcn. of results are given.

H. S. BAILEY

Lubrication (MOORE) 13. The preparation, properties and testing of petroleum lubricants (KISSLING) 13. Pennsylvania lubricating oils as against others (ANON) 13. Separation of aromatic from non-aromatic compounds (U. S. pat. 1,441,341) 10.

Gasoline from fuel oil. E. M. HVARR. U. S. 1,445,688, Feb. 20. Fuel oil is treated with Cl gas at a temp. somewhat below the cracking point under pressure. The HCl thus produced is withdrawn and the treated oil is then further heated under pressure to effect cracking. The vapors are withdrawn and condensed and the condensate is fractionated.

Apparatus for cracking hydrocarbon oils. J. H. ADAMS. U. S. 1,445,281, Feb.

13. Horizontal cracking chambers are arranged in tiers connected in series extending through the walls of a furnace with removable closures for their ends. Collecting pans fit in the chambers at the bottom and steam pipes extend through the end with perforated portions longitudinally placed above the pans, for supplying superheated steam. Oil under pressure is continuously supplied to the lower end of the series and vapors are drawn off from the upper end of the series to a condenser which is maintained under pressure.

Apparatus for cracking hydrocarbon oils. S. L. GARTLAN. U. S. 1,445,433, Feb. 13. Texas fuel oil or similar oils are vaporized under approx. atm. pressure and the vapors are subjected to compression and later to sudden expansion and liquefaction.

23—CELLULOSE AND PAPER

CLARENCE J. WEST

A few high spots in the chemistry of cellulose. GUSTAVUS J. ESSHLEN, JR. *Ind. Eng. Chem.* 15, 306-8(1923).—Review under the headings: compn., lignocellulose, properties of cellulose, fermentation.

C. J. WEST

Preparation and properties of cellulose solutions. P. WAENTIG. *Papier-Fabr.* 20, 359-61(1922); *J. Chem. Soc.* 122, I, 988.—Viscose solns., suitably prepd., do not change so quickly as Cu solns. Cellulose, artificially prepd., is very sensitive to time, temp., and method of bleaching, and to treatment with acids and alkalies. Heating with dil. alk. solns. increases the viscosity of viscose solns. The changes in viscosity are conditioned by colloidal as well as by chem. changes. It may be assumed that there is a difference in constitution between cotton and artificial cellulose, the latter probably consisting of mol. aggregates of differing sizes. Treatment with boiling dil. alk. solns. results in a simplification of larger aggregates and a soln. of smaller aggregates.

C. J. WEST

Colloid chemical problems of the paper and cellulose industries. R. SIEBER. *Kolloid-Z.* 31, 308-10(1922).—A brief statement of some of the colloid chem. problems, such as beating, filling, etc.

C. J. WEST

Andropogons as paper-making materials. CH. GROUND. *Papier* 25, 446-9(1922).—*Imperata arundinaceae*, from Indo-China (14% of H₂O when air-dry), was steamed for 1 hr. under low pressure, and cooked for 7 hrs. with 13% of NaOH as a 5° Bé. liquor, under 3-3.5 kg. per cm.². Washing and defibering were carried out simultaneously. Bleaching in the cold in slightly acid soln. required 16% of bleaching powder, on the wt. of the pulp. Bleaching was satisfactory, except for the presence of some colored shives. The grass contained 42% of cellulose, and the yield of bleached pulp was 31%. The stock was engine sized with rosin, and a small amt. of starch was used as filler. The paper was of a fine white color; thickness 0.11 mm.; wt. 80 g. per m.²; breaking length, machine direction 3,166 m., cross direction 2,000 m., av. 2,583 m.; bursting strength 1,130 kg.; resistance to crumpling, machine direction 30, cross direction 11.7, av. 20.8. The fiber length of the cellulose 1-3.5 mm., av. 1.8 mm., av. diameter 0.01 mm., felting power 1/180. The fibers are regular, cylindrical, with sharp and elongated ends. The pulp is suitable for the manufacture of fine papers (printing, ledger), either alone, or preferably mixed with wood, rag, or bamboo pulps. Leaves (contg. a few fragments of stems) of *Andropogon muricatus* were cooked: (1) with 7% NaOH as a 4° Bé. liquor, under 3 kg. per cm.², for 4.5 hrs., which gave a decidedly greenish yellow material; (2) with a 3° Bé. Ca(HSO₃)₂ liquor, for 4.5 hrs., under 3 kg. per cm.², which gave a light yellow product. Yield of bleached pulp 35%. The paper obtained was of fairly good quality, white, opaque, but not very strong. The fibers are 1.5-2 mm. long.

and 0.010–0.015 mm. in diameter, felting power 1/150. The finished pulp still contains about 20% of non-fibrous material which accounts for the lack of strength.

A. P.-C.

Developments in the use of bleaching agents for textiles and paper pulp (INMAN) 25.
Cellulose chemistry (HINZERT, HILL) 10.

ANDRÉ, LOUIS EDGAR: Die Fabrikation der Papiermaché- und Papierstoff-Waren. 2nd Revised ed. Vienna & Leipzig: A. Hartleben. 395 pp. M 72.

ANDRÉ, LOUIS EDGAR: Papier—Spezialitäten. 2nd Revised and enlarged ed. Vienna & Leipzig: A. Hartleben. 334 pp. M 96.

BERSCH, JOSEF: Zellulose, Zelluloseprodukte und Kautschuksurrogate. 2nd Revised ed. Vienna & Leipzig: A. Hartleben. 239 pp. M 72.

"Acetose" (acetylcellulose). J. O. ZDANOWICH. U. S. 1,445,382, Feb. 13. Cellulose, *e. g.*, in the form of cotton paper, is treated with an acetylating agent and a weak condensing agent such as Ac_2O and glacial AcHO until a thick paste is obtained and the latter is then subjected to the action of a strong condensing agent such as H_2SO_4 and additional glacial HOAc in order to complete the acetylation. The product may be used for artificial silk.

Solubilizing ketonic chlorides from cellulose. A. R. DE VAINS. U. S. 1,445,495, Feb. 13. Ketonic chlorides formed by the action of Cl upon ligno- or pecto-cellulose are rendered sol. by treatment with alk. solns. obtained by lixivation of cellulosic materials with alk. lyes.

Treating waste sulfite liquor. J. S. ROBESON. U. S. 1,445,603, Feb. 13. Sulfite cellulose waste liquor as it comes from a digester or storage tank is sprayed into air to effect oxidation and some evapn. with removal of free SO_2 . Calcined magnesite or other suitable reagent is then added to neutralize acidity and the liquor, freed from any ppt. which forms, is evapd. to 1.26 sp. gr. or to dryness. This treatment produces a product of strong adhesive properties, free from such alterations as may occur from undue heating, and adapted for fermentation to produce alcohol.

Viscose; artificial silk; films. H. DREYFUS. Brit. 183,882, Feb. 9, 1921. CO_2 in the abstract in C. A. 17, 209 should read CS_2 .

Coating for paper. H. N. CASE. U. S. 1,445,387, Feb. 13. A paper coating mixt. is formed of clay 39 lbs., H_2O for the clay 28 lbs., gelatin 74 oz., H_2O for the gelatin 15 pints, a 10% NaOH soln. 90 cc. and coloring material, *e. g.*, *p*-nitroaniline red.

Apparatus for testing paper and paper-board. W. D. LABATT and H. SENGEBUSCH. U. S. 1,445,964, Feb. 20. Mechanism is provided for regulating the stroke of a reciprocating plunger which compresses liquid against an elastic diaphragm pressing on the sample being tested.

24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

The formation of poudre B pastes. AB-DER-HALDEN. *Mem. poudres* 19, 154–60 (1922).—A study was made of the relations between the proportions of sol. and insol. nitrocellulose (CP2 and CP1), and of the solvent, and the plasticity of the resulting paste (*colloid*) in the manuf. of *smokeless powder* (Poudre B). The plasticity was measured by the method described in C. A. 17, 472. With 40% CP2, the plasticity increased uniformly as the amt. of solvent used increased (from 100 to 200% solvent). With either more or less than 40% CP2, plasticity increases at first very slowly; then rapidly

as the solvent is increased, the curves for plasticity showing an abrupt rise. Up to the max. amts. of solvent ever used in practice (140-150%) the coeff. of plasticity was greater with 40% CP2, than with any other proportion in the nitrocellulose mixt. If the content of CP2 is increased without sufficient increase of solvent, all of the CP1 is gelatinized but a part of the CP2 remains undissolved, a uniform paste is not produced, and a low plasticity results. In the mixing process the CP2 at first dissolves and this soln. then gelatinizes the CP1. Hence, a paste of normal plasticity requires (1) sufficient solvent to dissolve the CP2, and (2) such proportion of CP1, that the gelatinization of the latter is complete. Complete soln. of CP2 alone under the conditions of the test required 230% solvent.

C. G. STORM

Utilization of the coefficient of gelatinization (of nitrocellulose) in the mixing operation. SUPPIN. *Mem. poudres* 19, 161-3(1922).—Variations in the coeff. of gelatinization (cf. C. A. 16, 2990-1) of nitrocellulose used in the manuf. of *Poudre B* were found to be due to variations in the N content of the sol. nitrocellulose (CP2) used in mixt. with insol. nitrocellulose (CP1). A curve of actual results shows that for efficient gelatinization the %N should be between 11.8 and 11.9%. Higher values cause a lower coeff. of gelatinization, with tendency toward a dry, brittle *colloid*, even when excessive amts. of solvent are used.

C. G. STORM

Behavior of nitrocellulose on heating under pressure. A. LOGOTHETIS AND G. GREGOROPoulos. *Z. ges. Schiess-Sprengstoffw.* 17, 89-90(1922).—The use of steam under pressure for stabilizing nitrocellulose was resorted to during the War in order to save time and fuel. A rotating spherical autoclave of 8 cu. m. capacity was used, the steam entering and leaving through the hollow shaft. The nitrated product, after drowning, was given five 3-lr. washings at 90°, then placed in the autoclave with 4 times its wt. of H₂O and given several 2-hr. heatings with steam at 10-15 lbs. pressure (115-120°). Tables of results show that sol. nitrocellulose of about 12.40% N is more quickly stabilized than insol. nitrocellulose with 13.0% N. Decrease in N content is very gradual at 15 lbs. but much more rapid as the pressure is increased. At 40 lbs. the N fell from 12.40% to 11.22% with five 2-hr. heatings. The fibrous structure of the nitrocellulose is also gradually broken down by heating at higher pressure than 15 lbs., a powdery product resulting which still shows good stability at 135° but has a somewhat lower explosion temp.

C. G. STORM

Study of the pyroxylin sporting powder T. MAURICE PORCHÉ. *Mem. poudres* 19, 300-21(1922).—Data are given on pressures and velocities in different calibers and forms of fowling pieces of value to sportsmen and to makers of firearms and sporting powders.

CHARLES E. MUNROE

Influence of humidity on the ballistic qualities of BSP and US₂ powders. CHEVERREAU. *Mem. poudres* 19, 168-80(1922).—This gives the results of a comparative study of the hygroscopic properties of a standard type of French and of a U. S. smokeless powder, and of the effect of the various amts. of H₂O absorbed on the ballistics of these powders.

CHARLES E. MUNROE

Liquid oxygen in mining. ALFRED JAMES. *Bull. Inst. Mining Met.* No. 221, Feb. 1923, 13 pp.—This is a critical review of data on the use of LOX at the Real del Monte Mines, Pachuca, Mexico (C. A. 17, 881) with an historical resumé. In 1917, there were 72 plants, varying in capacity from 5 to 110 l. of liquid O per hr., installed at coal mines, 56 plants, of 7-256 l., installed at metal (chiefly Fe) mines, and 32 plants, of 5-75 l., installed at potash mines. The consumption of liquid O for explosive purposes in Germany in 1917 was 23,000,000 l. It is claimed that 1½ l. of it equals 1 kg. of dynamite in efficiency.

CHARLES E. MUNROE

The use of explosives with liquid oxygen in the iron mines of Lorraine. DUVIVIER, *et al.* *Rev. ind. minière*, Supplement Dec. 1, 1922, 84 pp.—A general treatise on liquid-

O explosives, including an historical survey, an illustrated description of the process, the economic, technical and hygienic advantages and numerous expts. and results with such explosives. C. C. DAVIS

Explosives in liquid-air rectification plant. ERNEST FYLEMAN. *Chem. Ind.* **42**, 152(1923).—A continuation of discussion on previous paper (C. A. 17, 1147). The necessity for keeping an oil-lubricated air compressor, feeding a liquid air plant, cool and for taking the most stringent precautions to avoid any possibility of C_2H_2 entering the compressor from without cannot be too strongly insisted on or too widely known.

CHARLES E. MUNROE

The chemical engineer's part in the rescue work at the Argonaut mine disaster. L. H. DUSCHAK. *Chem. Met. Eng.* **28**, 349-50(1923).—With pictures of the gas-sampling app. used and an account of the methods of analysis employed, a description is given of the manner the progress of the fire some thousand feet underground was followed and subdued until it became possible for the rescue crews to enter. Also there is shown the method of estg., from the results obtained in the analyses of the gas in the exhaust fan discharge, the extent of shaft timbering burned. CHARLES E. MUNROE

The Springfield gas explosion. W. L. WEDGER. *Fire and Water Eng.* **73**, 296-8, 307(1923).—The explosion occurred in the purifying house of Springfield (Mass.) Gas Light Co. It appears that a purifying box on the 2nd floor started to "blow" at the water seal, that the relief valve, or "distributor," was stuck, and that beside the purifying room was an elevator shaft inclosing elevators operated by d. c. motors and having a manhole in the floor of the pent house. The elapsed time from the first blowing of the water seal to the explosion was estd. at 5-10 mins. W. estimates that 40,000-80,000 cu. ft. of the coal gas (sp. gr. 0.4) escaped in this interval and became mixed with the air. When the call for help to operate the "distributor" was made an employee went up on the elevator to the filter floor of the purifying house. As he stopped the elevator, raised the gate and stepped off, the explosion occurred. C. E. M.

Dust explosions—a colloidchemical process. P. BYERSDORFER. *Kolloid-Z.* **31**, 331-3(1922).—An "aerosol" of sugar dust explodes very easily but only then when the distance between the particles and their size makes it possible that through rapid motion the particles can accumulate a large elec. charge. Lightning on a small scale was observed in dust suspensions and dust explosions are probably caused by such spontaneous lightnings caused by the discharge of the accumulated charges on the dust particles. A. MUTSCHELLER

Preventive measures against dust explosions in coal mines. LOUIS DRESSAGNE. *Tech. moderne* **14**, 615-7(1922).—In a device for cleaning coal-mine galleries suction is created by means of an air blast, and the dust-laden air is bubbled through water contg. a trace of oil. The recovered dust can be used as fuel. A. P.-C.

Explosive (lead trinitroresorcinate). E. HERZ. U. S. 1,443,328, Jan. 23. $C_6H-(NO_2)_3O_2Pb$ is prepd. by adding a boiling soln. of $Pb(NO_3)_2$ 650 g. in 1.4 l. of H_2O to a boiling soln. formed from $(O_2N)_3CaI(OH)_2$ 245 g., cryst. Na_2CO_3 290 g., H_2O 12.8 l. and glacial $AcHO$ 77 cc. It is a granular cryst. powder of dark orange color, d. 3.09, very difficultly sol. in H_2O and is a powerful explosive, adapted for use in primers alone or with chlorate, perchlorate, nitrate, peroxide, permanganate, chromate, Sb sulfide, powd. glass or with TNT or Hg fulminate charges. Cf. C. A. 17, 1147.

Dynamite containing ammonium nitrate. C. A. WOODBURY. U. S. 1,445,378, Feb. 13. Blasting explosives of a "strength of 45-55%" are formed with 9-12% nitroglycerin and sufficient NH_4NO_3 to give most of the additional strength possessed by the explosive. An explosive of this type may contain: nitroglycerin 9-12, NH_4NO_3 45-66 and $NaNO_3$, wood pulp, etc., 25-43 parts.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

René Bohn (1862-1922). PAUL JULIUS AND M. A. KUNZ. *Ber.* 56, 13-30A (1923).—An obituary, with portrait and bibliography. E. J. C.

Coal-tar dyes. BABULAL, LALA GOVILA. *Jayaji Pratap, Birthday Number* (Reprint) 1921, 9 pp.—A short historical sketch is followed by a plea for the development of the coal-tar industry in India by capitalistic investment and with government aid. Tables show the usual products obtained by distg. coal, tar, light oils, and carbolic oils.

L. W. RIGGS

The present and the future in the manufacture of auramines. RAFFAELE SANSONE. *Color Trade J.* 10, 53-5, 119-21 (1922).—A discussion of the properties, fastness, dyeing methods and applications of auramines to cotton, wool, silk, paper and leather dyeing. This is followed by a description of the HCHO or Sandmeyer-Ferr process of manuf. and the app. required. The working of the plant, suggested improvements and chem. control, and the diphenylamine-phosgene, phosgene-ZnCl₂, and phosgene-S processes of manuf. are then described.

CHAS. E. MULLIN

The mercerizing, dyeing, and finishing of ramie. W. MARSHALL. *J. Soc. Dyers Colourists* 38, 293-9 (1922).—Two varieties of china grass, rhea, or ramie, *Boehmeria nivea* and *B. tenacissima*, are used for fiber. The processes of decortication, degumming and spinning and the properties of ramie are discussed. In mercerizing ramie the temp. rises slightly more than for cotton or linen. When the yarn is mercerized under tension it is brighter and less hairy in appearance. The fibers contract, swell, twist, increase in strength, luster, transparency and dyestuff affinity. Single fibers mercerized without tension lose luster and acquire a twist which is always absent in the original. Mercerized in the hank without tension, it loses some of its brightness and tensile strength, and contracts more than cotton or linen. When hank-mercerized under tension it loses hairiness, gains luster, strength, flexibility, elasticity and is less brittle. This also applies to mercerization in the piece. Ramie is no more difficult to dye than cotton and is penetrated equally well; the fastness to washing and light are equally good; in luster and smartness the mercerized yarn is far superior to the unmercerized yarn and is far ahead of mercerized cotton. Seven photomicrographs are reproduced.

CHAS. E. MULLIN

The production of woolen effects in piece-dyed woolen goods. F. MÜNZ AND R. HAYN. *Chem.-Ztg.* 46, 945-6 (1922).—The thoroughly dried woolen goods (8-15 kg.) are placed in 100-l. drum set in a large wooden vat contg. water. The reserve soln. is added. For 1 kg. undyed wool 1 l. Ac₂O, 4 l. glacial AcOH, 140 g. H₂SO₄ (100%), and 77 g. Me₂NPh are used. For 1 kg. of dyed wool 1 l. Ac₂O, 4 l. glacial AcOH and 60 g. H₂SO₄ are used. After the addition of the reserve soln. the drum is closed and rotated at the rate of 2 r. p. m. The inside temp. is raised to 58° in 1 hr. and maintained at this point for 1½ hrs. The reserve soln. is washed out and the wool thoroughly rinsed. This weak acid wash water obtained may be used in the dye vats for acid and chrome colors. In the case of undyed wool it is simply dried. Wool already dyed is treated with 20% Cr(OAc)₃ (20° Bé.) and 4% HCO₂H (85%) for ¼ hr. at 75°, then washed and dried.

C. T. WHITE

Effects of waterproofing materials and outdoor exposure upon the tensile strength of cotton yarn. H. P. HOLMAN AND T. D. JARRELL. *Ind. Eng. Chem.* 15, 236-40 (1923).—In the expts. described, unbleached and unsized warp yarn was treated with various waterproofing materials and exposed to the weather to show the effects on tensile strength. After one year's exposure the treated yarn was in most cases stronger than the untreated yarn after exposure, but weaker than the treated

yarn before exposure. With 3 treatments contg. asphalt there was no material loss in tensile strength. Raw drying oils caused more deterioration than the same oils previously boiled with metallic driers. Semi-drying and non-drying oils, in most cases, caused as much deterioration as the raw drying oils. The addition of burnt umber to a drying-oil treatment had a marked preservative effect. Results on yarn were not strictly applicable to woven fabrics.

L. W. RIGGS

Efficacy of a centrifuge for removing surface liquids from cotton hairs. H. F. COWARD AND LEO SPENCER. *J. Textile Inst.* 14, 28-32T(1923).—The centrifuge designed to the authors' specification had an effective diam. of 8.2 cm. and was motor-driven at rates up to 8000 r. p. m. At the max. rate its centrifugal acceleration was 2000 times that of gravity. Trials were made at various speeds maintained for various times with cotton wet, resp., with water, 20.1% NaOH, 48.8% NaOH, alc., xylene and other liquids. A few min. centrifuging at max. speed removes the interfibrillar liquid down to 5 to 10% of the wt. of the fibers themselves, except in the case of extremely viscous liquids such as castor oil. Since cotton retains water after centrifuging up to 50% of its wt., and NaOH solns. up to nearly 300% of its wt., practically all of these liquids are held within the body of the cotton hairs. Absorption of caustic soda solutions by cotton. *Ibid* 32-45T.—Detns. were made of the compn. of the solid phase when cotton, free from the bulk of its so called impurities, is immersed in NaOH solns. of various strengths, and also when the cotton is subsequently washed in other strengths of the same alkali or in water. The expts. of Gladstone, Vieweg, Miller and Leighton are reviewed. With the aid of a suitable centrifuge the authors have made what they believe to be the first direct detn. of both the water and the NaOH present in the alkali satd. fiber. Detailed descriptions are given of expts. made to det. the following points: (1) H₂O and NaOH absorbed by loose cotton fibers, (2) H₂O and NaOH absorbed by a cotton fabric, (3) preferential absorption of NaOH in fiber and in fabric, (4) H₂O absorbed by cotton (fiber) after removal of NaOH, (5) hysteresis in the absorption of NaOH solns. The results of these detns. are assembled in 5 tables of figures and are illustrated by 9 charts of curves. The curves for total NaOH absorbed are complex and give no indication of the formation of definite chem. compds., nor are they of the form commonly found for simple adsorption. The preferential absorption of NaOH by loose fiber is approx. proportional to the concn. of the soln. in contact with the cotton. In this case also there is no evidence of the formation of definite compds., but the form of the curves is not inconsistent with the view that compds. of the general formula (C₆H₁₀O₂)_n.(NaOH)_n are formed. Cotton hairs swell to an increasing extent, as the % of NaOH rises, up to a limit of nearly 3 times the original vol. This limit is reached at about 14.3% NaOH and no further swelling occurs in stronger alkali. It is concluded that the cuticle of the fiber is responsible for this limitation, since the contents of the fiber are capable of much greater swelling when not restrained by cuticle. Similar results are obtained with cotton hairs in yarn or fabric except that the max. swelling is then much less because of the constraint imposed by the fabric as a whole on the individual hairs. There is a general parallelism between the technical results of mercerization and the swelling deduced from the expts. The expts. are also made to account for the superior results obtained in mercerizing yarn as compared with mercerizing cloth. The residual swelling in fiber which has been mercerized and washed is shown to be closely proportional to the absorption of benzopurpurin 4B, as measured by Knecht; and the diminished swelling of such fibers on soaking in water after drying has been correlated with their well known diminished "affinity" for dyestuffs after drying. Marked hysteresis in the shrinkage of cotton fiber on replacement of mercerizing solns. by weaker solns. has been observed, and the results give a reason for the necessity in technical operations for retaining cloth under tension until almost the whole of the NaOH has been removed.

L. W. RIGGS

Developments in the use of bleaching agents for textiles and paper pulp. W. M. INMAN. *J. Soc. Chem. Ind.* **41**, 368-71T(1922).—An interesting historical sketch of bleaching is given with special reference to the use of liquid Cl. L. W. RIGGS

BARKER, A. F.: Textiles. Revised ed. London: Constable. 398 pp. 15s.

LEDERLIN, P.: Blanchiment, Teinture, Impression, Apprets. Paris: J. B. Bailière et Fils. 543 pp. F. 55 net.

ZERR, GEORG AND RÜBENCAMP, ROBERT. *Handbuch der Farbenfabrikation*. 3rd Ed. revised and enlarged. Berlin: Ullstein. 908 pp.

Monoazo dyes and lakes. A. LINZ. U. S. 1,445,331, Feb. 13. Lakes which when printed are clear and brilliant are obtained from monoazo dyes which have been converted into alkali bisulfite compds. before conversion into lakes. E. g., the Na salt of the monoazo dye "red for lake D" may be treated with NaHSO_3 and the product pptd. from the clear solu. formed by addition of NaCl . A temp. of 90-100° is suitable for reaction between the azo dye and NaHSO_3 . After the preliminary treatment, the lake is formed by combination with "gloss white," BaCl_2 and NH_4OH .

Yellow vat dyes. G. KALISCHER, J. MÜLLER AND D. NISSON. U. S. 1,440,833, Jan. 2. Yellow vat dyes are prepd. by heating 2-methylantraquinone with S and aromatic compds. contg. the *p*-diamine nucleus, e. g., benzidine, *p*-nitroaniline, *p*-phenylenediamine, *p*-aminoazobenzene or their chloro substitution products. The dyes obtained are insol. in H_2O and in most org. solvents. With alkali hyposulfites they yield olive to brown vats from which vegetable fibers are dyed greenish to reddish yellow shades, fast to washing, Cl, acids and light.

Chromium compounds of azo dyes. F. STRAUB. U. S. 1,440,566, Jan. 2. Hydrated Cr oxide, KOH and H_2O are heated with glycerol, gallic acid, glucose or various saccharides, phenols, tannins, cellulose derivs. or lignins and the products are further heated with azo dyes. Blue-violet, violet and red dyes are obtained, which on wool are fast to light and fulling.

Ornamental patterns on mercerized fabrics. W. WARR. U. S. 1,445,734, Feb. 20. A washed and dried mercerized fabric is dampened, portions of the fabric are subjected to friction and pressure in order to cause them to be dyed a deeper shade and the fabric is subsequently dyed.

Silk goods dyed in the piece. J. SEYER. U. S. 1,446,860, Feb. 27. Silk goods, dyed in the piece and fast to washing in lukewarm soapy H_2O but not fast to boiling aq. soapy liquid, are prepd. by diazotizing a dye on the goods and then treating with a boiling aq. soln. of Na_2HPO_4 , Na_2SO_4 , Turkey-red oil, soap and dye.

Treating silk. C. W. COLB, JR. U. S. 1,446,834, Feb. 27. Silk is successively treated with a Sn soln., washed, dried, treated with a glycerol soln., "thrown," woven and dyed.

Sodium oleate in viscose. H. J. HEGAN. U. S. 1,446,301, Feb. 20. Na oleate 0.2% is used in viscose prepd. from cotton for making threads or filaments, in order to reduce the tendency to vesiculation or globulation which would produce uneven threads.

27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

Smalley Foundation of the A. O. C. S. Progress report on coöperative meal series. H. C. MOORE. *Cotton Oil Press* **6**, No. 9, 33-4(1923).—Results on NH_3 and oil in 12 cottonseed meals by 58 and 40 analysts, resp., indicate that better agreement is being obtained than ever before. H. S. BAILEY

Analysis and discussion of results on crude-oil and iodine-number coöperative samples of the A. O. C. S. H. J. MORRISON. *Cotton Oil Press* 6, No. 8, 33; No. 10, 31; No. 11, 31-2(1923).—Results on refining losses and I no. by 30 chemists on 4 samples of crude cottonseed oil. These indicate the necessity for a more definite statement in the official A. O. C. S. method of the details of the refining procedure. H. S. BAILEY

The oil, fat and wax laboratory of the Bureau of Chemistry and its relation to the vegetable-oil industry. G. S. JAMIESON AND W. F. BAUGHMAN. *Cotton Oil Press* 6, No. 9, 30-1(1923).—A history of the lab. including brief abstracts of some of its more important researches. H. S. BAILEY

Reversion of color in coconut oil. E. W. LAZZELL. *Cotton Oil Press* 6, No. 9, 35(1923).—A coconut oil pressed from sun dried Solomon Island copra partly damaged by sea water, bleached to 25 yellow 3.3 red. After standing 4 days in a glass bottle in the lab. its color was 54 yellow, 9 red. Acidity of the sample was 6.5% as oleic. H. S. BAILEY

The extraction of seed oils by means of acetone. LOUIS PÉRIN. *Industrie chimique* 10, 63-5(1923).—The extn. is carried out on the same principle as extn. in a Soxhlet, 6 extns. being usually sufficient. The advantage of Me_2CO as a solvent resides in its affinity for water, which is greater than its affinity for the oil to be extd. After extn. the oil and solvent sep. into 2 layers, the upper consisting of Me_2CO and H_2O (from the seeds) and contg. a certain amt. of dissolved oil, and the lower consisting of 88-90% of the extd. oil with a certain amt. of Me_2CO . The layers are treated separately with H_2O , the total amt. of H_2O being about 10% of the total amt. of Me_2CO to be rectified. By a method (not described) about 40% of the Me_2CO is retained within the cycle and does not require to be redistd. P. calcs. that the coal consumption should be about 150 kg. per ton of seeds treated. A. P. C.

Solubility tests for castor oil. H. S. BAILEY. *Cotton Oil Press* 6, No. 9, 35-6(1923).—The Frahot test (soly. of castor oil in petr. ether at 20°) is the most reliable for the detection of adulteration in castor oil. It is essential that the detn. on unknown samples be checked by controls with pure castor oil because of the variation in the solvent action of different gasoline. At 20° gasolines with boiling ranges of 35-50°, 50-65°, 65-80°, 80-100° and 100-125° dissolved, resp., 1.53, 2.00, 2.33, 3.52 and 4.06 g. of castor oil per 100 cc. of soln. The 50-65° petr. ether held 2.66 g. of oil in soln. at 30° and 4.76 at 40°. Detns. of the I nos., acetyl and acid values and n_{25} of the portions of oil extd. by successive washings with 35-60° gasoline showed a gradual decrease in the I no. and acetyl value and increase in the n_{25} with each successive ext. The acetyl value of the first ext. was 20 to 30 points lower than that of the original oil; low enough in the case of both an "Oriental" and an "English Cold Pressed" oil to have condemned it as adulterated. Cf. Trevithick and I. auro, C. A. 17, 646. H. S. BAILEY

Fractionation of oils in hydraulic pressing. A. F. SIEVERS AND J. D. MCINTYRE. *Cotton Oil Press* 6, No. 10, 28(1923).—To det. if there is any difference between the first and last oil flowing from a hydraulic pressing of cottonseed, samples were collected at 7 intervals during 7 individual pressings. Analyses of these 49 samples for color, sp. gr., n_{25} , free fatty acids, sapon. no., and I value indicate: (1) the color and n_{25} increase slightly toward the end of the pressing; (2) variation occurs in the % of free fatty acids, sapon. and I nos. but without any relation to the various fraction; (3) the cup refining losses were lowest with the first 2 fractions but the absolute oil method showed most neutral oil in the last fraction; (4) a fuller's earth bleach on the last fraction, after refining, did not give quite so light a color as with oils obtained earlier in the pressing. H. S. BAILEY

Behavior of vegetable oils with copper acetate. W. H. DICKHART. *Cotton Oil Press* 6, No. 11, 32-3(1923).—Crude vegetable oils, with the exception of cottonseed,

give a green gasoline soln. when shaken with aq. $\text{Cu}(\text{OAc})_2$. None of the 18 refined oils tested produced any color. This is proposed as a method for detecting adulteration (1% or more) of crude cottonseed oil with other oils. Method: Shake vigorously 10 g. of crude oil with 150 cc. of gasoline, h. p. below 65°, and 40 cc. of a 5% $\text{Cu}(\text{OAc})_2$ soln. After the two solns. have sep'd. draw off the gasoline layer, filter and compare with a blank made on a known pure cottonseed oil having nearly the same acidity as the sample. An editor's note states the method has been tried in his lab. and that there is danger of suspecting adulteration when none is present owing to the formation of Cu soaps with high acid oils which give a green gasoline soln. Also in *Am. J. Pharm.* **95**, 108-9(1923).

H. S. BAILEY

A miniature coconut and its oil, *Jubaea chinensis*. C. A. LATHRAP. *Cotton Oil Press* **6**, No. 8, 32(1922).—The nuts of *Jubaea chinensis* or *spectabilis*, are 60% shell and 40% meats. The meats contain 68% oil and 27% solids not fat, moisture 5%. Analysis of the pressed cake: N $\times 6.25 = 21\%$, ether ext. 8, crude fiber 11, ash 3, carbohydrates 48, moisture 8%. The pressed oil had d_{25}^{25} 0.9243, n_{25} 1.4541, free fatty acids (as oleic) 0.2%. Sapon. no. 273.7, I no. (Wijs) 12.7, R.-M. value 8.8, Polenski no. 25.5, unsaponifiable 0.24%, m. p. 11-12°, Lovibond color 15 yellow 1.5 red, titer 18.7°, n_{25} of solid acids 1.4400, of liquid acids 1.4441. I no. (Wijs) of liquid acids 41.2.

H. S. BAILEY

Report on methods for examination of cacao butter. W. F. BAUGHMAN. *J. Assoc. Official Agr. Chem.* **6**, 101-6(1922).—The critical temp. dissolution test for detecting coconut, palm-nut and cottonseed oils, tallow or stearins, corn oil, peanut oil, etc., and the $\text{Me}_2\text{CO}-\text{CCl}_4$ test for hydrogenated cottonseed oil, tallow oleostearin and paraffin were studied by collaborators. Further study is recommended. Results and details of methods are given (cf. *C. A.* **16**, 1876).

H. A. LEPPER

Determination of moisture in check meals (cottonseed). L. M. TOLMAN. *Cotton Oil Press* **6**, No. 11, 30-1(1923).—A study of the wide variation in the procedure for detn. of H_2O in oil meals as shown by replies from 75 analysts reporting on the A. O. C. S. collaborative samples indicates great need for more uniformity. Many different types of ovens are in use, temps. ranging from 95° to 110° are used and the time of drying varies from 45 min. to 16 hrs. Results at temps. of 95-100° were in no better agreement than those at 100-105° or 105-110°. On one sample the difference between the max. and min. H_2O was 4.1% on a total moisture of about 9%. On nearly all the 20 samples there was a difference of at least 1%. A special committee of the A. O. C. S. to study moisture detns. is urged.

H. S. BAILEY

Refractometer value of oil mixtures. C. M. VISMAN. *Olieën, Vetten en Oliezaden* **7**, 361(1922).—Observations made at 40° with a Zeiss-Abbe refractometer upon mixts. of oils agree within 0.1° with previously computed values. NATHAN VAN PATTEN

Oil milling in the Orient. A. O. FRENCH. *Cotton Oil Press* **6**, No. 10, 35-9(1923).—An interesting account of F.'s trip through Japan, Manchuria, China, P. I., India, Ceylon, and Egypt. The story is illustrated with cuts of Oriental oil plants and the various methods of crushing copra, etc., are described.

H. S. BAILEY

Oil blowing method and equipment. J. H. ANDERSON. *Cotton Oil Press* **6**, No. 10, 27(1923).—Great care is required in the blowing of rape, corn, castor, and soy-bean oil to prevent too much darkening, or thickening. After the crude, well filtered oil has been heated to the desired temp. and the blowing air turned on usually no more heating is required. In many cases it is necessary to cool by running cold water through the coils. The viscosity is tested by the time it takes a 0.25-inch steel ball to fall through a 10-in. depth of oil. The fumes from the blowing kettle are best gotten rid of by passing them through a condenser and burning the uncondensed residue under the factory boilers.

H. S. BAILEY

Carbon removes mineral oil bloom. J. H. ANDERSON. *Cotton Oil Press* 6, No. 10, 33(1923).—Several tanks of crude cottonseed oil, shipped in cars previously used for tar, when refined showed the characteristic color and bloom of mineral oils. This was completely removed by treatment with a bleaching carbon. Many additional tests of carbon for the removal of mineral oil indicate that it is always successful but that the off color in cottonseed oils due to bad seed cannot be taken out with chars.

H. S. BAILEY

Boring (cutting) oils. H. MAYER. *Seifensieder Zig.* 49, 422, 437, 449(1922).—M. describes the mfg. of cutting oils of 0.885–0.900 sp. gr., mixed with emulsifying agents, such as sulfonated castor oil or caustic alkali and olein, rosin, rosin oil, NH_3 and alc. Detailed directions and recipes are given. The oils are used in the form of emulsions contg. 5–30% of the oil.

P. ESCHER

The action of sodium silicate when used in soaps. I. The detergent value of sodium silicate. A. S. RICHARDSON. *Ind. Eng. Chem.* 15, 241–3(1923).—The H_2O softening action of $\text{Na}_2\text{O} \cdot 2.83 \text{ SiO}_2$ in the presence of Na oleate is greater at higher temps. and with waters high in Mg salts. The detergent action of silicate is dependent on fatty acids in the dirt but is not proportional to the soap formed. The drop no. of Na oleate soln. is increased by the addn. of $\text{Na}_2\text{O} \cdot 2.83 \text{ SiO}_2$ but not as much as by that of Na_2CO_3 (cf. following abstr.).

WM. STERICKER

The value of silicate of soda as a detergent. I. WM. STERICKER. *Ind. Eng. Chem.* 15, 244–8(1923); cf. preceding abstr.—Saponifiable and, to some extent, mineral oils are emulsified by Na silicates. The emulsifying power increases as the ratio of SiO_2 to Na_2O increases. Suds and emulsions formed with soap are stabilized by Na silicates. The more siliceous ones are more effective than Na_2CO_3 . $\text{Na}_2\text{O} \cdot 0.3 \text{ SiO}_2$ alone and with soap was used to wash greasy overalls.

WM. STERICKER

Extracting oil from vegetable meals. M. WHITEHEAD. U. S. 1,446,606, Feb. 27. Crushed seed meal or similar oil-bearing material is intimately mixed with a solvent and the material and solvent are moved countercurrentwise continuously through an extr. app. which subjects the material to intermittent wringing and to a final solvent vaporization.

Apparatus for pressing oil from seeds or similar materials. N. B. HENRY. U. S. 1,445,314, Feb. 13.

28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

Some fungi from the air of sugar mills and their economic importance to the sugar industry. P. A. VAN DER BIJL. *S. African J. Sci.* 18, 232–3(1922); cf. *C. A.* 16, 849.—Petri dishes with suitable media were exposed for 15 min. around the sugar mill and in a sugar store room. The following organisms were identified: *Cladosporium* sp., *Penicillium divaricatum* and 4 other species *Aspergillus flavus*, *A. parasiticus*, *A. repens-glaucus* group, and *Monilia* sp. These fungi are among those which are known to cause sugar deterioration.

F. W. ZERBAN

Juice clarification. H. EGETER. *Arch. Suikerind.; Mededeel. Proefstat. Java-Suikerind.* 1922, 337–50.—This is a general discussion, from the modern physical-chem. point of view, of the objects and the mechanism of clarification, and of the means by which it is or may be accomplished.

F. W. ZERBAN

Determination of the true Brix degrees of molasses by calculation. CHAS. MÖLLER. *Intern. Sugar J.* 24, 635–7(1922).—It is often necessary in sugar-house calcs. to use the true, instead of the apparent, Brix. From exams. of many hundred samples of molas-

ses was established an empirical relationship between the true and apparent values of the total solids. For the same factory and the same mode of manuf. the ratio between the true and apparent Brix of the discarded molasses is $(AB - TS)/(TB - TS) = \text{const.}$; AB and TB are the apparent and true Brix values, and TS is the true sucrose. A table is given showing the const. as established for 3 factories during 10 yrs. of operation. It is possible to calc. the true Brix in functions of the true sucrose and of the apparent Brix, by the formula $TB = [(AB - TS)/\text{const.}] + TS$. W. L. OWEN

Remarks on filtration. H. EGGER. *Arch. Suikerind.; Mededeel. Proefstat. Java-Suikerind.* 1922, 323-36.—Filtration practice is still largely empirical. For filter presses, assuming a circular cross section for the pores of the cake, theoretical formulas can be derived on the basis of Poiseuille's law. Such formulas are developed mathematically for the following three cases: (1) the particles of the ppt. are non-compressible and non-elastic; (2) they are non-compressible, partly elastic and partly non-elastic (this applies to the cane sugar industry); (3) they are all elastic. In each of these cases the formulas are developed for const. pressure, for const. vol. of filtrate, and for the pressure increasing continuously as a function of the time. In four practical tests in a sugar factory, where the pressure and all other conditions were kept const., the amt. of filtrate obtained equalled $C\sqrt{T}$, where C is a const. and T the time. F. W. ZERBAN

The optical analysis of starch sugar sirup. OTTOMAR WOLFF. *Chem.-Zig.* 46, 1101-3(1922).—Several graphs are given by which the solids can be calcd. from the reading of a soln. in the Lowe interferometer (*C. A.* 5, 1211) and the dextrose from the polarization. From these values dextrose in sirup can be calcd. No analytical results are given but results as satisfactory as those obtained by reduction methods are claimed. The procedure is not directly applicable to dry starch-sugar. H. A. LEPPER

Investigation on the dissemination of the yellow stripe disease by lice. G. WILBRINK. *Arch. Suikerind.; Mededeel. Proefstat. Java-Suikerind.* 1922, 413-56.—The observation of Brandes, that yellow stripe disease is spread by *Aphis adusta*, has been confirmed for the form of the disease prevalent in Java. Ordinary grasses serve as host plants, and it is therefore important to keep the fields free from weeds. Selection of plant material and use of resistant varieties are also effective in keeping the disease down. F. W. ZERBAN

The value of NH_4Cl as nitrogenous fertilizer (KUYPER) 15. Ammonium sulfate-nitrate and urea as nitrogenous fertilizers (KUYPER) 15.

AUDEN, H. A.: Starch and Starch Products. Pitman's Common Commodities and Industries Series. London: Sir Isaac Pitman & Sons, Ltd., 121 pp. 3s.

Continuously operating air-pressure filter. J. W. BROWN. 1,446,448, Feb. 27. The filter comprises filter-cloth sections laid over screen wire, and is adapted for filtering beet-sugar juices.

29—LEATHER AND GLUE

ALLEN ROGERS

The determination of nitrogen in leather. R. E. PORTER, H. C. REED, AND G. W. SCHULTZ. *J. Am. Leather Chem. Assoc.* 18, 51-2(1923).—It is suggested that the official method of the Am. Leather Chem. Assoc. be changed to require the use of 1.5 instead of 0.7 g. of finely divided leather in detg. N, the object being to get a more representative sample. J. A. WILSON

Purity of tanning materials. C. R. OBERFELL. *J. Am. Leather Chem. Assoc.*

18, 52-4(1923).—An objection to the use of the term "purity" to designate the ratio of tannin to nontannin in tanning exts. The ratio is important, but the term misleading.

J. A. WILSON

The synthesis of the depsides and the tannins. HARRY HEPPWORTH. *J. Soc. Chem. Ind.* 42, 41-3T(1923).—A brief review, particularly of the work of Fischer and Freudenberg (cf. *C. A.* 8, 345, 2702; 15, 52).

J. A. WILSON

The colorimetric estimation of pyrogallol, gallotannin and gallic acid (MITCHELL) 7. The hydrolytic decomposition of glutins and glue testing methods (GERNGROSS, BRECHT) 2.

ALEXANDER, JEROME: Glue and Gelatine. Monograph of Am. Chem. Soc. New York: The Chemical Catalog Co., Inc. 230 pp. \$3.00.

HUC, P.: Manuel du tanneur, mégissier, corroyeur. Paris: J.-B. Baillière and Sons. 402 pp. Fr. 12.

LAMB, M. C.: The Manufacture of Chrome Leather. London: The Anglo-American Technical Co., Ltd. 450 pp. 26s.

30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

Report of committee D-11 on rubber products. F. M. FARMER, *et al.* *Proc. Am. Soc. Testing Materials* 22, Pt. 1, 486-93(1922).—Recommendations for acceptance and for revisions (cf. *C. A.* 16, 768) are made.

C. C. DAVIS

Rubber softeners. P. M. AULTMAN AND C. O. NORTH. *Ind. Eng. Chem.* 15, 262-4(1923).—A study of the comparative action of 20 softeners on cured rubber, particularly in their depolymerizing action. Data show the time for disintegrating cured rubber at 140°. Oils with a low I no. dissolve rubber much more rapidly than those with high I no. Blown oils act more slowly than the same oils untreated. Addn. of accelerators and of S in most cases to the liquid hastens disintegration. By measuring the increase in wt. of cured rubber in the liquids, the swelling power was also detd. The rapidity of disintegration is a function both of the rate of swelling and of the rate of depolymerization of the rubber aggregate. Addn. of S and of accelerators to the liquid increases the swelling power. Reinforcing pigments retard swelling in proportion to their vol., but independently of their nature. Mixts. of softeners with appreciable quantities, but softeners with no disintegrating action mixed with disintegrators prevent the action of the latter. The higher the state of cure, the lower the rate of depolymerization.

C. C. DAVIS

Thermal changes during vulcanization. IRA WILLIAMS AND D. J. BEAVER. *Ind. Eng. Chem.* 15, 255-8(1923).—A method is described for detg. the intensity of energy changes during cure. When rubber is heated with S, there is at first an evolution of a small amt. of heat. Heat liberated during cure is probably due to the rubber-S reaction, since no liberation of heat could be detected in reactions between rubber and accelerator, S and resin or S and accelerator. A slight absorption of heat occurs toward the end of the rubber-S reaction. The velocity of this reaction increases with the temp., with the % S and by addn. of accelerators.

C. C. DAVIS

Natural and artificial aging of vulcanized rubber. C. PELIZZOLA. *Giorn. chim. ind. applicata* 4, 458-60(1922).—Artificial (accelerated) aging of vulcanized rubber is completely identical with natural aging, from the chem. as well as from the physico-mechanical point of view. Accelerated aging tests to control exptly. the behavior of

definite mixts. under conditions of aging are hence dependable. The action of ultra-violet rays upon crude and vulcanized rubber increases the oxidation. R. S. P.

Proposed revisions of the tentative specifications for cotton rubber-lined fire hose for private fire department use. F. M. FARMER, *et al.* *Proc. Am. Soc. Testing Materials* 22, Pt. I, 494-6(1922).—Certain changes are recommended (cf. *C. A.* 16, 768). C. C. DAVIS

Comparative investigations of the toxicity of some samples of benzene and particularly of solutions of rubber in benzene (PUGLIESE) 13. Experimental investigations of the toxic action of benzene, petroleum ether and toluene (PUGLIESE) 13. Di-substituted guanidines (SCOTT) 10.

GEER, WM. C.: *The Reign of Rubber*. New York: The Century Co. 344 pp. \$8.00. Reviewed in *Ind. Eng. Chem.* 15, 305(1923).

SIMMONS, H. F.: *Rubber Manufacture*. London: Library Press. 146 pp. 25s.

Vulcanizing rubber. S. M. CADWELL. U. S. 1,445,621, Feb. 20. Thiuram disulfide derivs. contg. substituted alkyl and aryl groups are used as accelerators in vulcanizing rubber with S.

Vulcanization accelerators. S. M. CADWELL. U. S. 1,440,961, Jan. 2. Metal alkyl xanthates are used as accelerators with S at ordinary vulcanizing temps.; if used with aniline, vulcanization may be effected at lower temps., even approx. ordinary room temps. The accelerator may be used to the amt. of about 4-5% the wt. of the rubber. U. S. 1,440,962 describes the use as vulcanization accelerators of a large no. of derivs. of thiocarbonic, thiocarbamic, thioacetic, thiohenzoic, thiobutyric acids and thiourea. The derivs. include esters, metallic salts and substituted NH₂ compds. Some of these compds. even in as low an amt. as 0.1% of the rubber enable vulcanization to be effected rapidly. U. S. 1,440,963 and 1,440,964 also relate to the use of these compds. as accelerators.

Dehydrating raw rubber. S. C. DAVIDSON. U. S. 1,446,737, Feb. 27. See Brit. 179,622 (*C. A.* 16, 3414).

Plastic products from dechlorinated oils. H. A. GARDNER. U. S. 1,446,039, Feb. 20. "Dechlorinated oils" (cf. U. S. pat. 1,384,447; *C. A.* 15, 3758) are employed with S and rubber to produce tough molded articles which may be vulcanized, *e. g.*, tire-treads, shoe-soles, laminated waterproof fabrics or coating for paper. Fillers or pigments may be added, *e. g.*, lampblack, ZnO or BaSO₄.

